6. TRANSPORT AND FATE OF CHEMICAL PARAMETERS OF INTEREST

"Transport and fate" refers to the movement of contaminants in the environment, their alteration during movement, and their ultimate destination. In line with federal guidance, this chapter describes the transport and fate of the main chemical parameters of interest (CPOIs) based on the contaminants and stressors of concern identified in the Onondaga Lake Baseline Ecological Risk Assessment and Human Health Risk Assessment (TAMS, 2002a,b) summarized in Chapters 7 and 8 of this Onondaga Lake Remedial Investigation (RI) report. These CPOIs have been grouped for the purposes of this discussion of transport and fate based on similar spatial distributions within the lake and on similar geochemical properties. This yielded the following eight groups:

- Mercury and methylmercury.
- Other metals.
- Benzene, toluene, ethylbenzene, and xylene (BTEX) compounds.
- Chlorinated benzenes.
- Polycyclic aromatic hydrocarbons (PAHs).
- Polychlorinated biphenyls (PCBs).
- Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/PCDFs).
- Calcite.

Mercury and calcite are discussed separately from the other CPOIs in this chapter because of their relatively unique geochemistries and historical importance to lake contamination. Reflecting this importance, extensive analyses of their transport and fate (including development of mass balance models) were performed by Honeywell and its consultants and were later revised by NYSDEC/TAMS during the RI. Mass balance models were considered for other CPOIs, as required in the RI/FS Work Plan (PTI, 1991c). To this end, estimates were made to quantify the sources and sinks of other CPOIs (see Section 6.2).

This chapter is organized into five sections, with the first three describing, respectively, the transport and fate of mercury and methylmercury, non-mercury CPOIs, and calcite in Onondaga Lake. The fourth section presents the estimated inventories (masses) of select CPOIs in lake sediments. The last section summarizes the transport and fate of CPOIs in Onondaga Lake.

6.1 Transport and Fate of Mercury and Methylmercury in Onondaga Lake

The purpose of this section is to describe the transport and fate of mercury and methylmercury in Onondaga Lake, describing in detail the process used to derive each estimate of mercury load into the lake and its environs. Mercury and methylmercury are discussed together here, as their chemistries are inherently related. Wherever relevant, this section is consistent with NYSDEC's Revision of the Onondaga Lake Mercury Modeling Report (NYSDEC/TAMS, 1998b).

The discussion of mercury loads is focused on the 1992 period of stratification, May 25 through September 21, 1992 (NYSDEC/TAMS, 1998b). This stratification period was selected because extensive data on water column concentrations, tributary loading, and water column processes are available. In addition, this stratification period is also a period of relatively constant hydrologic discharges (steady stream flow), and so represents a distinct phase in the hydrodynamic regime of the lake. This period presents a logical time frame for mass balance estimation.

Inputs, which are discussed below in Section 6.1.1, include precipitation, tributary flow, groundwater and porewater advection, diffusive flux from porewater, and methylmercury production in the water column. Previous attempts by Honeywell to calculate annual inputs were determined to be unsupportable with the available data, since those data did not cover an entire year and, in particular, did not cover the spring turnover/high tributary flow period of the lake (NYSDEC/TAMS, 1998b).

Section 6.1.2 addresses the transport and fate of mercury in the water column of Onondaga Lake during stratification and during fall turnover. Mass balance estimates of total mercury and methylmercury were developed for the stratified period. Section 6.1.3 discusses releases from the Honeywell in-lake waste deposit, as introduced in Chapter 4, Section 4.5. Section 6.1.4 discusses the deposition of mercury and other metals to lake sediments based on high resolution sediment cores.

Prior to discussing mercury fate and transport, it is useful to briefly describe the lake's limnological conditions, as these conditions strongly influence mercury transport. During summer stratification, the lake's thermocline strongly resists vertical mixing in the lake. Ignoring internal seiches, the typical depth of the thermocline is about 9 m. This impediment to transport commonly results in two distinct chemical environments and provides a logical boundary for segmenting the lake. Wind-driven horizontal mixing in the epilimnion is adequate to keep the epilimnion vertically well mixed. On the other hand, there are no strong forces (e.g., wind) that function to mix the hypolimnion. The hypolimnion is rather stagnant and quiescent, which allows particles to permanently settle and concentration gradients to form in the water column.

Wagner et al. (2002) documented that sustained wind events can result in the transport of hypolimnetic waters to the surface waters of Onondaga Lake during the stratified period. A wind along the long axis of the lake builds up epilimnetic waters in the far end of the lake (a seiche), and to maintain a water balance in the lake, the hypolimnetic water upwells to the surface at the windward end of the lake. On September 11, 2002, over a period of 11 hours, Wagner et al. (2002) monitored a wind event with average speed of about 10 m/s along the main (long) axis of the lake. This wind event resulted in an upwelling event. Wagner et al. (2002) reported that the hypolimnion lost one-third of its methane inventory to the surface waters. Dissolved oxygen (DO) concentrations of less than 1 mg/L were documented in the surface waters at the windward end of the lake. Based on reviews of historic weather, lake stratification, and water quality data, Wagner et al. (2002) noted that at least eight such upwelling events have occurred between 2000 and 2002.

A mass balance approach was used to quantify the transport and fate of mercury in both the epilimnion and hypolimnion. The epilimnion is bounded by the air-water interface at the top, the thermocline and shallow sediments at the bottom, and tributaries and the lake outlet at the sides. The hypolimnion is bounded by the thermocline at the top and deep sediments at the bottom. During stratification, the hypolimnion is essentially isolated from all external water flows (i.e., tributary flows).

In addition to the period of stratification in 1992, data were also obtained to describe lake turnover conditions in fall 1992 and fall 1999. In early fall, cooler air temperatures and generally higher wind speed serve to cool and deepen the epilimnion. In response, the depth of the thermocline begins to drop lower in the lake. As the thermocline drops, formerly hypolimnetic water is incorporated into the epilimnion until the temperature difference between the epilimnion and hypolimnion is eliminated. At this point, the lake is isothermal and essentially completely mixed from top to bottom. This is referred to as fall turnover.

6.1.1 Inputs of Total Mercury and Methylmercury to Onondaga Lake

In this section, mercury inputs to the water column from external sources (i.e., across "system boundaries") are discussed and quantified. This discussion focuses on the period of stratification from May 25 through September 21, 1992; however, fall turnover data from 1992 and 1999 are also discussed. For the water column mass balance, boundaries at three surfaces are defined: the air-water interface, the sediment-water interface, and the water-water interface at the mouths of tributaries.

The initial Onondaga Lake RI/FS Work Plan (PTI, 1991c) identified several potential sources of mercury to Onondaga Lake, including the tributaries, the Metropolitan Syracuse Sewage Treatment Plant (Metro), groundwater advection, porewater diffusion, porewater advection, and precipitation. The work plan detailed investigations intended to describe the mercury loads from these sources based on concepts and mechanisms documented in other aquatic systems. These sources of mercury to Onondaga Lake are described in this RI as those "sources identified in the RI/FS Work Plan." However, in the course of the investigation additional sources were identified, including resuspension and potential advection of materials (i.e., sediments and waste) from the Honeywell in-lake waste deposit and the enhanced release from the profundal sediments caused by the production of dissolved-phase mercury and by methane gas ebullition. These sources are referred to in this RI as "sources in addition to those identified in the RI/FS Work Plan" or "additional sources."

Inputs of total mercury and methylmercury to Onondaga Lake were quantified based on data obtained during this RI, as follows:

- Direct precipitation to the lake surface.
- Tributary flow and discharges from Metro.
- Groundwater advection.
- Porewater diffusive flux from sediments.
- Dissolved-phase release from sediments.

- Hypolimnetic accumulation.
- Net methylmercury production in the water column.

6.1.1.1 Direct Precipitation to the Lake Surface

The input of total mercury and methylmercury to Onondaga Lake via direct precipitation to the lake surface was estimated from rainfall rates (National Oceanic and Atmospheric Administration [NOAA], 1992), the surface area of the lake, and an assumed concentration for total mercury and methylmercury in precipitation. A total volume of 5.5×10^6 m³ of precipitation was estimated from the NOAA data for the stratification period.

The average concentration of mercury in precipitation was assumed to be 13 ng/L, based on data from the Mercury Deposition Network for a monitoring location at Sturgeon Point in Erie County, New York (National Atmospheric Deposition Program, 1998). The calculated average is based on weekly monitoring data from September 30, 1993 to December 31, 1995. Sturgeon Point, located on the shore of Lake Erie, is the closest location to Onondaga Lake on the network. Nonetheless, Sturgeon Point experiences different climate and meteorological conditions than the Syracuse area, where Onondaga Lake is located. Because of this, the sources of mercury to precipitation may differ between the two sites. Because of the large number of potential mercury sources in the Syracuse area, the Sturgeon Point value may underestimate the precipitation concentrations around Onondaga Lake. Unlike Syracuse, Sturgeon Point is relatively remote from local sources of mercury to the atmosphere.

The input of total mercury to the Onondaga Lake surface from precipitation is calculated to be 71 grams (g) for the stratification period. Several precipitation studies have shown that methylmercury is usually a small fraction of total mercury in precipitation (Bloom and Watras, 1989; Lee and Iverfeldt, 1991; Mason et al., 1997; Munthe et al., 1995). Assuming a fraction of 0.3 percent of total mercury (consistent with Mason et al., 1997), the amount of methylmercury deposited to the surface of Onondaga Lake by precipitation during the time period is estimated to be 0.2 g.

6.1.1.2 Tributary and Metro Loads

Total mercury and methylmercury inputs from the tributaries and Metro to Onondaga Lake were estimated for the stratification period from the combined data collected in 1992 by Honeywell/PTI (PTI, 1993c) and Driscoll (pers. comm., 1995). Honeywell/PTI measured total mercury and methylmercury concentrations, as well as tributary flow rates, in each major tributary and Metro effluent twice a month from April through December 1992. Driscoll (for Syracuse University) measured total mercury concentrations periodically in Ninemile Creek, Onondaga Creek, Ley Creek, and the Metro effluent from February through August 1992.

A detailed discussion of the data and methods used to estimate loading rates is provided in Appendix H. In summary, the FLUX model (Walker, 1987) and refinements to the model were used to assess the relationship between concentration and flow for each tributary, and determine the appropriate methods of estimating concentrations between samples. For most tributaries, there is no significant relationship between flow and concentration. Daily loads were estimated for the stratification period. The 95 percent confidence intervals for the loads were estimated using the bootstrap resampling technique (Efron, 1982).

Tables 6-1 and 6-2 show the estimated tributary and Metro loads of total mercury and methylmercury to Onondaga Lake from May 25 through September 21, 1992. The mean mass of total mercury discharged to Onondaga Lake is estimated to be 2,510 g, with the 95 percent confidence interval ranging from 2,110 to 2,970 g. Approximately 51, 14, and 24 percent (a total of 89 percent) of the estimated total mercury input from tributaries was discharged by Ninemile Creek, Onondaga Creek, and Metro, respectively. The remaining 11 percent of tributary input was attributed to Ley Creek, Harbor Brook, Tributary 5A, and the East Flume. The contribution of total mercury from Ninemile Creek is significantly higher than the contributions from the other tributaries during the stratification period. Mercury contributions to Ninemile Creek are primarily attributed to Honeywell releases.

The mean mass of methylmercury discharged to Onondaga Lake from May 25 through September 21, 1992 is estimated at 116 g (about 5 percent of the total mercury load), with the 95 percent confidence interval ranging from 95 to 141 g. Approximately 42, 18, and 36 percent (a total of 96 percent) of the estimated methylmercury input from tributaries was discharged by Ninemile Creek, Onondaga Creek, and Metro, respectively. The remaining 4 percent of tributary input was attributed to Ley Creek, Harbor Brook, Tributary 5A, and the East Flume. The contribution from Metro is expected, as physical and chemical conditions in sewage treatment plants are suitable for the formation of methylmercury, and this formation within Metro was observed by McAlear (1996) in a study of total mercury and methylmercury concentrations and fluxes within the plant.

The Honeywell (PTI)/Driscoll results can be compared to those of Gbondo-Tugbawa (1997), who determined fluxes of total mercury and methylmercury to Onondaga Lake in 1995 and 1996; however, as Gbondo-Tugbawa's loadings were estimated on an annual basis, only the relative contributions can be compared directly. Gbondo-Tugbawa (1997) reported a combined 94 percent of the total load of total mercury originating from Ninemile Creek, Onondaga Creek, and Metro, which is consistent with the 89 percent contribution from these sources estimated for the period from May 25 to September 21, 1992, based on the Honeywell (PTI)/Driscoll data.

For methylmercury, Gbondo-Tugbawa (1997) reported a combined contribution of 89 percent from Ninemile Creek, Onondaga Creek, and Metro, with Metro contributing about 44 percent of the estimated annual load. These results are consistent with the observations based on the Honeywell (PTI)/Driscoll data described above, although the loadings estimated in this RI during the stratification period suggest that Ninemile Creek produced slightly higher loads of methylmercury relative to Metro as compared to the results obtained by Gbondo-Tugbawa (1997).

6.1.1.3 Groundwater Advection

Regional and site geology and hydrogeology are described in Chapter 3, Sections 3.3 and 3.6, respectively. Studies conducted to date suggest that groundwater influences are dominated by inflow from shallow hydrogeological systems bordering the lake. Hydrologic investigations conducted at the Willis Avenue site show that, along the shoreline, water levels in wells installed at multiple depths indicate a vertical gradient upward toward the lake, suggesting that the shoreline is an area of groundwater discharge to the lake (Figure 6-1). Thus, groundwater discharge will likely occur along the shoreline where flow paths are vertically upward. Assuming the regional gradients along the shoreline are relatively consistent, the amount of groundwater entering the lake will be primarily controlled by the hydraulic conductivity and thickness of the hydrogeological sediments that underlie the southern shoreline, or margin, of the lake.

The input of total mercury and methylmercury from groundwater through sediment was determined for the littoral zone and profundal zone. The littoral zone is defined here as sediments and water at water depths shallower than the summer thermocline (9 m), and the profundal zone as sediments and water at depths greater than 9 m.

The estimation of mercury input across littoral sediments to the epilimnion is based on the conceptual model of groundwater from upland sites moving through preferred pathways, not chemically interacting with the sediments, and discharging to the epilimnion. There are two major assumptions to this scenario. The first is that the discharge of water from the littoral sediments is primarily based on the upland groundwater regime. It is possible that additional groundwater discharge is entering the lake from deeper formations, and the groundwater estimate based on the upland sites is biased low. It is also possible that the groundwater gradient, and thus discharge rate, may be lower in the area of the shoreline near the lake outlet.

The second assumption is that the mercury concentrations in the groundwater are not affected by interactions with the sediments. The behavior of mercury in contact with solids (either soil or sediment) is complex, and is further complicated in this instance by the fact that the material in front of the Wastebed B/Harbor Brook site (and perhaps at least partially in front of the Semet Residue Ponds and Willis Avenue sites) is actual waste material, which can act as a source of mercury itself.

However, for the purpose of estimating the load of mercury to the lake, the practical issue is whether the mercury concentrations change between the groundwater and the porewater. In front of the shoreline area between Harbor Brook and Tributary 5A, there are three cores (from Stations S344, S402, and S405) from the 2000 sampling event in which total mercury and methylmercury concentrations in porewater were determined. The porewater mercury concentrations in the three cores varied greatly, both horizontally and vertically, although there was a consistent increase in the porewater mercury concentrations as the depth into the sediments increased. The average mercury concentration for these data was 7,700 ng/L (standard deviation = 11,700), which is not significantly different from the average groundwater total mercury concentration of 5,000 ng/L determined for the monitoring wells (not hydropunches) in the fill layer in the Wastebed B/Harbor Brook site. This suggests that the concentrations of mercury in water entering the lake

are similar to those observed for local groundwater. In turn, this suggests that the load calculated based on the data from the upland sites is comparable to the load actually entering the lake.

The mass loading of mercury was estimated by separating the lake into three general areas:

- The littoral shoreline area between Harbor Brook and Tributary 5A.
- The remaining littoral lakeshore area.
- The profundal zone.

The littoral shoreline area between Harbor Brook and Tributary 5A was divided into three areas (i.e., Semet Residue Ponds, Willis Avenue, and Wastebed B/Harbor Brook) for the purposes of characterizing the mercury concentrations and hydraulic gradients. Specifically, the groundwater flux for the littoral zone of the lake was estimated by using the detailed information available from the shoreline area between Harbor Brook and Tributary 5A to produce estimates of water and mercury loads to the lake for that area.

A mercury load for the remaining shoreline area of the littoral zone was estimated by using the water fluxes for the shoreline area between Harbor Brook and Tributary 5A and a background groundwater concentration for mercury.

For discharge across profundal sediments to the hypolimnion, the input was estimated from the concentrations of mercury in sediment porewater and advective velocities estimated from the porewater chloride profiles. Further discussion of the estimation of groundwater fluxes is provided below.

Littoral Groundwater Loading of Total Mercury from the Lakeshore Area between Harbor Brook and Tributary 5A

A simplified two-dimensional analysis was performed to estimate the groundwater discharge and mercury loading to Onondaga Lake from Honeywell sites including the Semet Residue Ponds, Willis Avenue, and Wastebed B/Harbor Brook along the shoreline between Harbor Brook and Tributary 5A. The analysis was conducted using site-specific data for each of the three sites. Site stratigraphy was constructed from the original well logs for the area using the Groundwater Modeling System (GMS) software (http://www.bossintl.com/html/gms, accessed July 2002), with five distinct units identified (i.e., fill, Solvay waste, marl, sand and silt, and sand and gravel) in the unconsolidated materials above the till and bedrock. These units have varying thicknesses, depths, and, in some cases, horizontal extent. Pump test data collected in 2001 by O'Brien & Gere (2002f) for Honeywell from the Semet-Willis area were used to calculate the hydraulic conductivities for the fill, marl, sand and silt, and sand and gravel units. Slug test results from the wells on the Semet and Willis sites were used to calculate the hydraulic conductivities for the fill, marl, sand and silt, and Semet sites were used for the Solvay waste (Blasland and Bouck, 1989). Data from the Willis and Semet sites were used for the corresponding units on the Wastebed B/Harbor Brook site, since aquifer pump tests have not been performed at this site.

The mercury loading via groundwater advection in this area of the lake (about 5,000 ft of shoreline) was estimated to be 190 grams/month (g/mo) (64 g/mo from the Willis Avenue site, 77 g/mo from the Wastebed B/Harbor Brook site, and 47 g/mo from the Semet Residue Ponds site), or a total of 760 g for the lake during the stratified period. Details of the calculation of the advection loading from the individual site areas along the Honeywell shoreline (i.e., Willis Avenue, including the I-690 storm drains, Wastebed B/Harbor Brook, and the Semet Residue Ponds sites) are given below.

Willis Avenue

The data for the Willis Avenue site were taken from Wells WA-1, WA-2, WA-3, WA-4, WA-5, WA-6, WA-7, TW-2, OW-8, and OW-9 (Figure 6-2).

Two different methods were used to estimate the groundwater discharge in the unconfined aquifer (i.e., the fill), as follows:

- The first method was based on Darcy's equation, which assumes the hydraulic gradient to be linear. The estimated groundwater discharge for the fill using Darcy's equation was approximately 9,700 ft³/day.
- The second estimate was based on the Dupuit equation, which assumes the hydraulic gradient to be parabolic, due to lack of a confining layer at the top of the fill. The estimated groundwater discharge for the fill using the Dupuit equation was approximately 11,100 ft^3/day .

Table 6-3 presents the summary of the groundwater discharges and loadings from different units at the site.

The mercury loading to the lake via groundwater was calculated by multiplying the groundwater discharge by the concentration in the wells for different layers in the aquifer, except for the fill layer. For the fill layer, the mercury concentrations from the I-690 storm drain pipes (Outfall 41) were considered as an additional, single well location and included in the calculation of the average well concentrations for this layer. The groundwater concentrations for the different hydrogeologic units at the three sites are presented in Table 6-4. On the basis of the data, it is necessary to decide which probability distributions to use. The Shapiro and Wilks test (Gilbert, 1987) was used to determine whether the groundwater concentration data set has a normal or lognormal distribution. To the extent that the data appeared lognormal, the mean value was estimated using a minimum variance unbiased estimator (MVUE) given by Gilbert (1987). Otherwise, a simple arithmetic mean value was used.

Although the highest mercury concentration occurred in the marl, the groundwater discharge rate for that layer is very low; thus, the layer did not yield a large mercury loading to the lake. The highest concentration occurred in Well WA-7I (166 μ g/L), which is located near the center of the former Willis Avenue plant site, an area containing mercury dense non aqueous phase liquid (DNAPL). However, near the lakeshore, the concentrations in the marl reduced dramatically to about 0.5 μ g/L (Well WA-3I). The mercury loading to

the lake from the marl was only about 0.53 g/mo (Table 6-3). The total mercury load for this area was estimated at 64 g/mo, or 260 g for the period of stratification.

Semet Residue Ponds

The stratigraphy along the lakeshore for the Semet Residue Ponds site was taken from Figure 3 of the Pumping Tests report for the Semet Residue Ponds and Willis Avenue Sites, Geddes, New York (O'Brien & Gere, 2002f). Only Darcy's equation was used to calculate the groundwater discharges in the fill layer, due to the lack of information on the hydraulic gradient. In addition, from the geologic cross section perpendicular to the shoreline (Figure 4 of O'Brien & Gere, 2002f), it appears that the fill layer ends at the Solvay Wastebed A approximately 300 ft from the shore. Mercury concentration data from the Semet Residue Ponds site are limited. There are no mercury data from monitoring wells for the fill and the marl layers at the site. However, groundwater from the fill unit infiltrated the I-690 storm drain pipes (Outfall 40), and mercury concentration includes a very high reported value of $3.9 \ \mu g/L$ (see Table 6-5). Note that this average concentration includes a very high reported value for mercury at $15 \ \mu g/L$. Since the data appear to be lognormal, the minimum variance unbiased estimator (MVUE) of the mean concentration was used. Using the MVUE, the average concentration was $3.4 \ \mu g/L$ (see Table 6-4). Lacking any other data, the mercury concentration from Outfall 40 was used in the mercury loading estimation for the fill layer in front of the Semet Residue Ponds site.

The estimated groundwater discharges and mercury loadings to the lake in front of the Semet Residue Ponds site are presented in Table 6-6. The estimated load of 47 g/mo corresponds to 190 g for the stratified period.

I-690 Storm Drains

The storm drain system for the segment of I-690 that runs through the Willis Avenue and Semet Residue Ponds sites is divided into two sections, as follows:

- A western section that drains the area in front of the Semet site and discharges through Outfall 40.
- An eastern section that drains the area in front of the Willis site and discharges through Outfall 41.

Prior to the interim remedial measures (IRMs) conducted from 1996 to 1999, these pipes leaked and groundwater infiltrated into the pipes (O'Brien & Gere, 2002b). Thus, the pipes acted as a preferential pathway for the shallow aquifer (fill layer) to discharge to the lake. This discharge is not in addition to the flow through the fill aquifer, but represents a portion of the load from the fill unit. However, this discharge provides an opportunity to independently verify the estimates for groundwater transport from the entire fill unit, which is estimated to provide the bulk of the mercury load from the Willis Avenue site to the lake. This

verification can be achieved by comparing the load calculated from the two-dimensional model based on aquifer measurements for the Willis Avenue site discussed above, to a load that can be estimated using the direct measurements of flows and mercury concentrations in the pipes at Outfall 41 in front of the Willis Avenue site.

The cross-sectional area intersected by the I-690 storm drains was estimated to be 2,000 sq ft (a 500-ft distance [Figure 6-2 inset], from drain 45 to drain 41, 4 ft into the water table). For the first estimate, it was assumed that the pipe was not affecting the water table, and the hydraulic gradient between Wells WA-7S and WA-1S was used. The mercury loading from I-690 storm drains using these assumptions was estimated to be 29 g/mo.

If it is assumed that the presence of the pipes does affect the water table, and the pipe is located two-thirds of the distance (*l*) from Well WA-7S (see Figure 6-2 inset), the hydraulic gradient becomes 0.04 ft/ft. The mercury loading from the I-690 storm drains using this assumption is about 50 percent higher (45 g/mo versus 29 g/mo).

Table 6-7 shows the calculation for the mercury loading estimate from the pipes based on the aquifer measurements. The mercury concentration was taken from the average value of Outfall 41 (Table 6-8). This load corresponds to 120 g for the stratified period.

Using the mercury concentrations from Table 6-8 and the flow in the I-690 storm drains, a third estimate of the loading can be calculated independent of the aquifer-based assumptions. Honeywell is required to monitor the I-690 drains for flow and water chemistry, and to submit the results of this monitoring to NYSDEC on a quarterly basis. Flow was measured in the eastern drain system for April and May 1997 as part of this program. The flows for April never varied, even though there were several significant rainfalls for that period, suggesting that these data are suspect. The data for May showed changes in flows in response to rain events. Only the base flow in the pipes represents groundwater infiltration, since higher flows are attributed to surface runoff. For the following estimates, both the average base flow for the entire month of May (12.4 gallons per minute, or 67.6 m³/day) and the low flow toward the end of the May (5.1 gallons per minute or 27.8 m³/day, which may better represent the base flow during the drier period of the lake stratification) were used. Using these values, the mercury loads are estimated as:

- 1.01 g/day, or 120 g of mercury for the stratified period, based on 67.6 m^3/day .
- 0.42 g/day, or 50 g for the stratified period, based on $27.8 \text{ m}^3/\text{day}$.

These values agree very well with the aquifer model prediction of 120 g for the I-690 discharge during the stratified period.

The model's validity may be further confirmed by assessing the percentage of the fill load that may reasonably be expected to be carried by the pipes, based on cross-sectional areas. The fill at the downgradient edge of the Willis Avenue Plant site has a cross-sectional area of 8,500 sq ft, while the I-690

pipes could intercept the groundwater from an area of 2,000 sq ft. Thus, the pipes could intercept about 24 percent of the groundwater flow in the fill layer, based on area. The pipes carry 50 to 120 g out of a total for the fill of 250 g of mercury for the stratified period, or 20 to 48 percent of the mercury load. This is a reasonable agreement between the groundwater flows and the mercury loads, on a direct-comparison basis alone. However, since the region of the fill layer that is drained by the pipes appears to have higher concentrations of mercury than the rest of the fill unit (Well WA-1S, which is near the area drained by the I-690 pipes, has higher concentrations than Well WA-2S, which is east of that area), it is reasonable to expect that the groundwater flow carried by the pipes will have a higher percentage of the load. These comparisons indicate that the aquifer model is producing reasonable estimates of the groundwater mercury loads.

Wastebed B/Harbor Brook

The Wastebed B/Harbor Brook site stratigraphy was obtained from Figure 6 of the Harbor Brook Site Remedial Investigation/Feasibility Study Work Plan (O'Brien & Gere, 2002a). Due to lack of pumping tests in the Wastebed B area, the hydraulic conductivity values for the fill and marl layers were assumed to be the same as those for the corresponding layers from the contiguous Willis Avenue site. The hydraulic conductivity of Solvay waste was taken from the Hydrogeologic Assessment of the Allied Wastebeds in the Syracuse Area report (Blasland & Bouck, 1989). As was done for the Willis Avenue site, two different methods were used to estimate the groundwater discharge in the unconfined aquifer (i.e., fill layer). The estimated groundwater discharge for the fill using Darcy's and the Dupuit equations is approximately 17,000 and 17,500 ft³/day, respectively. Table 6-9 shows the groundwater discharges and mercury loadings for the Wastebed B/Harbor Brook area. The load estimated using the Dupuit equation corresponds to 77 g/mo, or 310 g of mercury for the stratified period.

The groundwater from the Wastebed B/Harbor Brook site discharges to littoral zone sediments, which are actually the Honeywell in-lake waste deposit. Three sets of porewater samples were collected from the deposit. These data allow an independent method of estimating the loadings from groundwater advection. Since the groundwater must pass through the waste to discharge to the water column, the discharge to the water column is essentially the groundwater with the changes to the mercury concentrations that occur within the wastes.

Mercury concentrations in groundwater were compared to mercury concentrations in porewater from lake sediments. The mercury concentrations in the groundwater at the Wastebed B/Harbor Brook site are presented in Table 6-4. The mercury concentrations for the porewater were taken from cores at Stations S344, S402, and S405, which were collected from the waste material in front of the Wastebed B/Harbor Brook site. Data from three different sediment intervals (0 to 4 cm, 4 to 8 cm, and a deeper interval [i.e., 60 to 64 cm for Station S344, 30 to 34 cm for Station S402, and 106 to 110 cm for Station S405]) were used to estimate the mercury loading using porewater concentrations (see Table 6-10).

The estimated mercury loading using porewater concentrations is presented in Table 6-11. The groundwater discharge used for this estimation is only from the fill layer at the Wastebed B/Harbor Brook

site (17,500 ft/day), because the hydraulic discharges through the Solvay wastes and the marl layers are very small. The upper and lower ranges of potential mercury loads based on porewater concentrations are included in Table 6-11. The average of these loadings is 115 g/mo, or 460 g for the stratified period, which is about 48 percent higher than the load calculated directly from groundwater flow at the Wastebed B/Harbor Brook site. These values are considered to be in good agreement with each other, but the larger flux estimated from the porewater calculation may suggest that the Honeywell in-lake waste deposit adds to the load carried by groundwater advection.

The groundwater loading from the shoreline between Harbor Brook and Tributary 5A of 760 g presented above enters the water column in the littoral zone of the epilimnion.

Alternative Groundwater Transport Mechanisms

An alternate hypothesis for a source of additional mercury loads via groundwater advection is a geographically small, but concentrated, source of mercury in an upland site that is mobilized by saline groundwater. To evaluate this hypothesis, NYSDEC/TAMS considered multiple possibilities, including that:

- There is elemental mercury DNAPL in Honeywell-related areas around the lake.
- Groundwater in some locations (e.g., the LCP Bridge Street site) has high chloride concentrations (exceeding 2,500 mg/L) that will enhance the dissolution of the elemental mercury and its subsequent transport into the lake.
- Groundwater with such high chloride concentrations will plunge through the thermocline under the influence of gravity.

The data sets available from wells from the upland sites were reviewed for a groundwater source with high chloride concentration as well as very high concentrations of mercury (i.e., on the order 40,000 to 50,000 ng/L of mercury or more). The possibility of such a source was evaluated as follows:

- On the upland sites of the Honeywell shoreline (Semet Residue Ponds, Willis Avenue, and Wastebed B/Harbor Brook sites), a combination of high chloride and high mercury concentrations is observed in specific locations on the Willis Avenue plant site. There is mercury DNAPL in the Solvay waste beneath the mercury cell building. Well WA-7I (screened in the marl) contained mercury at concentrations of 166,000 ng/L. However, these locations are in the marl and Solvay wastes, which tend to be very impermeable and transmit very little water. The effect of this is that wells along the shoreline and the I-690 storm drains do not contain mercury at concentrations above 20,000 ng/L.
 - The groundwater modeling calculations given above indicate that the majority of the total mercury load is transmitted through the fill formation. The fill formation

contains mercury at concentrations of between 3,000 and 7,000 ng/L and an average chloride concentration of 2,000 mg/L (ranging from 290 to 4,200 mg/L), which is not the combination of high chloride and mercury needed for this theory. The other formations all have higher chloride concentrations (15,000 to 50,000 mg/L) than the fill; however, they either have substantially lower conductivities and, thus, lower discharge rates than the fill, or they contain no mercury (Table 6-3). For example, the marl and the Solvay waste have permeabilities two orders-of-magnitude lower than the fill. In the sand and gravel formations, flow and chloride are sufficient but mercury is mostly non-detect. The Solvay waste groundwater may have the required chemical characteristics but insufficient flow. Thus, the data from the upland areas do not suggest that groundwater with extremely high concentrations of both mercury and chloride is entering the lake.

Chloride and mercury data in both sediment and porewater indicate that there is no sediment location with the high mercury/high chloride combination needed for this theory. Sampling in 1992 for chloride in sediment indicated that the porewater chloride profile contained relatively low concentrations of chloride (500 to 2,000 mg/L) throughout the lake, except for two locations: immediately in front of Tributary 5A and in front of Wastebeds 1 through 8. Both of these locations contain relatively low concentrations of mercury in the sediments (see Chapter 5, Figures 5-2 and 5-3). The three locations in the in-lake waste deposit where porewater concentrations of mercury were measured have highly variable mercury concentrations in porewater ranging from 9 to 34,300 ng/L. However, the chloride concentrations in the sediments in this area were all relatively low. Thus, the data from the sediments do not suggest a groundwater flow with extremely high concentrations of both mercury and chloride entering the lake.

The conductivity profiles from the 1999 turnover data indicate a peak in conductivity at water depths greater than 18.5 m on some sampling dates. However, these peaks were not consistent and no mercury data were collected from that depth. Sharpe and Driscoll (pers. comm., 2002) consistently monitored the 19 m depth in their profiling at the southern deep basin location and collected chloride and mercury data from that depth in 2000. In the October 16 and 23, 2000 samples, there was a distinct spike in conductivity and chlorides at the 19 m depth. However, the total mercury concentration was typical of the hypolimnion at that time (about 15 ng/L), and not indicative of an extreme mercury source. These data suggest that plunging inflows reach the bottom of the lake at times, but they do not contain extremely high concentrations of mercury, and their ephemeral nature suggests that they are event-related and not a consistent groundwater source.

• The Honeywell geophysical report (PTI, 1992a) noted that the side-scan sonar imaging showed several features in the lake that appeared to be "craters" on the order of 0.5 to 1 m across that could indicate either gas or fluid venting. In addition, the sub-bottom profiles captured several vents actively releasing material 6 to 8 m into the water column. It seems very unlikely that a dense groundwater seep would project that far upward into the water column. The most likely explanation of these features is the venting of methane gas from the profundal sediments, which was documented by Addess (1990), and is discussed in Section 6.1.1.5 below.

Given the information currently available, it is unlikely that a dense, mercury-contaminated groundwater source accounts for the increase in mercury inventory in the lake.

Littoral Groundwater Loading from the Remaining Lakeshore Area (Outside of the Tributary 5A to Harbor Brook Reach)

Both groundwater flow and mercury concentration must be estimated for the remaining lakeshore area, since there are no known direct measurements of these properties outside of the area between Harbor Brook and Tributary 5A. To estimate the quantity of groundwater flow from the remaining lakeshore area to the lake, it was assumed that groundwater flow conditions in the unconsolidated sediments at the Willis Avenue site are representative of average flow conditions around the lake. At the Willis Avenue site, the sand and gravel layer is highly permeable and supplies a large portion of the groundwater discharge, but is discontinuous. The typical discharge for the entire shoreline is, therefore, likely to be between the Willis Avenue site total discharge and the total without the sand and gravel layer.

The total groundwater discharge for the Willis Avenue site is 37,000 ft³/day, or 1,050,000 L/day. The groundwater discharge without the sand and gravel layer is 12,000 ft³/day, or 340,000 L/day for the 1,000 ft of shoreline in front of the site. On a per-foot of shoreline basis, these discharges with and without the sand and gravel layer translate to 1,050 L/ft-day and 340 L/ft-day, respectively. For the 120-day stratified period, the discharges are 1.26×10^5 L/ft of shoreline with the sand and gravel, and 4.1×10^4 L/ft of shoreline without the sand and gravel.

Total discharge equals the unit discharge multiplied by the length of shoreline of concern. The remaining lake shoreline is the total shoreline of approximately 59,000 ft minus the 5,000 ft of shoreline between Harbor Brook and Tributary 5A, or 54,000 ft. Based on 54,000 ft of remaining shoreline, the range of background groundwater discharged to the littoral zone of the lake is between 2.2×10^9 L and 6.8×10^9 L for the stratified period. On a daily basis, the estimated groundwater flow is between 18,000 and 57,000 m³/day, whereas the average daily flow of the major tributaries (Onondaga Creek, Harbor Brook, Ninemile Creek, and Ley Creek) and Metro for the period from 1983 to 1992 was 1,200,000 m³/day. Therefore, this estimate of groundwater flow suggests that about 3 percent of the total inflow to the lake is from groundwater, which is consistent with the previous analyses of groundwater and backflow additions to the lake (NYSDEC/TAMS, 1998b).

To calculate the mercury loading rates from groundwater to Onondaga Lake, it was necessary to estimate background concentrations of mobile mercury in groundwater, defined as the dissolved groundwater concentration.¹ These estimates of mobile mercury concentrations and the estimates of groundwater inflow rates were then used to estimate the loading rates of mercury in groundwater to the remaining lakeshore area. Based on a review of the existing analytical data, it was assumed that concentrations of mobile mercury are at background levels everywhere around the lake, except in the vicinity of the Honeywell sites.

Background dissolved mercury concentrations were estimated by reviewing data from the following studies:

- **Groundwater sampling conducted by Honeywell/PTI (PTI, 1993f) at the Solvay Wastebeds**. Filtered and unfiltered groundwater samples from 12 monitoring wells were analyzed for mercury using trace-metal clean techniques and cold-vapor fluorescence during two sampling rounds in 1992 (Table 6-12) (PTI, 1993f). Values for total mercury ranged from 1.8 to 50.7 ng/L. Total suspended solid (TSS) concentrations ranged from 4.2 to 4,120 mg/L for these samples, indicating that excess particulate matter was probably introduced into the well during purging. Because mercury adsorbed onto the TSS in these samples is unlikely to be mobile in groundwater, mercury concentrations in unfiltered samples are not representative of the mobile fraction. Samples from five wells were filtered at the analytical laboratory, and concentrations ranged from 0.9 to 11.4 ng/L, with a mean concentration of 5 ng/L.
 - Surface water sampling conducted by Honeywell/PTI (PTI, 1993c) during base-flow conditions in the unaffected tributaries (Bloody Brook and Sawmill Creek) on the northeast side of Onondaga Lake. Unlike the other streams that are tributaries to Onondaga Lake, water and sediments in Sawmill Creek and Bloody Brook are not believed to have been affected by local mercury sources. In addition, these two tributaries are "gaining streams" that receive discharge from surrounding groundwater. Total mercury concentrations in samples collected from Sawmill Creek and Bloody Brook on June 18, 1992, were 2 and 3.6 ng/L, respectively (PTI, 1993c). Dissolved concentrations in the streams were not measured as part of the external loading and flushing investigation. This sampling event was conducted during a dry period when rainfall had not occurred for nine days and flow rates were low (0.5 and 0.7 cubic feet per second [cfs], respectively). Therefore, at the time of sampling, base-flow conditions probably existed in these tributaries, so that flow consisted primarily of groundwater inflow. The concentrations of total mercury detected in Sawmill Creek and Bloody Brook during a rainy, high-flow sampling event on December 17, 1992, were higher (9.7 and 47.2 ng/L, respectively) than during the low-flow event, most likely reflecting the influence of surface water runoff and increased suspended solids on

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¹ It is possible that filtering may remove a portion of the mobile fraction of the mercury from the sample.

mercury concentrations. The tributary data indicate that the concentration of mobile mercury in groundwater on the less-developed northeast side of the lake is in the range of 2 to 4 ng/L.

Groundwater sampling data near a remote lake in northern Wisconsin (Krabbenhoft and Babiarz, 1992). The data from Sawmill Creek and Bloody Brook for mobile mercury in groundwater on the northeast side of the lake are similar to a mercury concentration in background groundwater reported by Krabbenhoft and Babiarz (1992) in a study of groundwater transport of mercury in and out of Pallette Lake, located in a remote area of northern Wisconsin. Using trace-metal clean techniques and low-level mercury analysis using cold-vapor fluorescence techniques, these investigators determined that background concentrations of dissolved mercury in groundwater surrounding Pallette Lake were in the range of 2 to 4 ng/L.

Based on the data described above, it was assumed that the ambient background concentration of mercury in groundwater is in the range of 2 to 11 ng/L, with a best-estimated value of 6 ng/L. The groundwater inflow and advective mercury load rates are presented in Table 6-13. Using the discharges based on the Willis Avenue site and the background mercury concentrations, the mercury loads from the non-Honeywell shoreline are estimated to be between 13 and 41 g for the stratified period, with a "best-estimate" average value of 27 g.

Estimation of Littoral Groundwater Loading of Methylmercury

Groundwater loading of methylmercury for the lakeshore area between Harbor Brook and Tributary 5A was estimated as follows:

- The average methylmercury concentration as a percentage of total mercury from porewater data at Stations S344, S402, and S405 around the Wastebed B/Harbor Brook area is 9 percent.
- Assuming that the above fraction of methylmercury is applicable to the groundwater load of mercury of 760 g during the stratified period, the load of methylmercury is estimated as 70 g.

For the remaining lakeshore area, background methylmercury concentrations were assumed to be similar to surface water methylmercury concentrations measured in Bloody Brook (0.047J ng/L, Appendix G1, Table G1-96) and Sawmill Creek (0.21J ng/L, Appendix G1, Table G1-97) during low-flow conditions in 1992. If the largest value, 0.2 ng/L, is used to represent the concentration of methylmercury in groundwater inflow to the remaining lakeshore areas, and using the discharges for the Willis Avenue site, the loading of methylmercury for the stratified period would be 0.4 to 1.4 g, with a best-estimate value of 0.9 g.

Porewater Advection to the Profundal Zone

The following analysis characterizes the significance of porewater advection in the profundal sediments. This calculation is based on the absence of dissolved-phase mercury production or release mechanisms in profundal surface sediments, and assumes that mercury migration through porewater occurs via the displacement of porewater via flow due to groundwater discharge. The magnitude of advection can be determined from concentration profiles of chloride in sediment porewater. Chloride is often selected as a hydrodynamic tracer because it is chemically conservative, thus isolating physical processes. Previous studies (Effler et al., 1990; Rowell, 1992) suggested that the chloride profiles in Onondaga Lake sediments are controlled by diffusion, which is consistent with the linear concentration gradient observed (Gillham and Cherry, 1982). However, more detailed insight into the physical processes can be gained by using the advection-dispersion equation for transport of non-reactive substances in porous media. By applying this equation to chloride in porewater, model predictions can be compared to observed chloride distributions, and the significance of physical processes (i.e., advection and diffusion) can be determined.

The advection-dispersion equation describes the transport of non-reactive solutes in a water-saturated porous medium due to the physical processes of advection, dispersion, and diffusion. The equation is commonly applied to groundwater transport of tracers to determine aquifer characteristics. Because the processes of molecular diffusion and hydrodynamic dispersion have the same effect on solutes, they can be represented in the same manner mathematically with a single variable that represents the sum of the processes. For one-dimensional transport, such as vertical transport in sediments, the equation is:

$$\partial C/\partial t = D(\partial^2 C/\partial z^2) - V(\partial C/\partial z)$$

where:

C=concentration at some depth z at time tD=diffusion/dispersion coefficientV=advective velocity.

As written in this equation, D and V include the effects of porosity and tortuosity. There are numerous solutions to this equation, based on initial and boundary conditions. The difference between the model used here and the model commonly used for assessing solute transport in groundwater is that the downstream boundary condition is not a concentration of zero at infinite distance, but the concentration at the sediment-water interface. For simulating the concentration of chloride in the sediments, a steady-state condition is assumed. The resulting steady-state analytical solution (Maris and Bender, 1982) is:

$$C(z) = C(0) + (C_{max} - C[0]) \times (e^{Z/Z^*} - 1)/(e^{Zmax/Z^*} - 1)$$

where:

C(z)	=	concentration at any depth (mg/L)
C(0)	=	concentration at the sediment-water interface (mg/L)
C_{max}	=	maximum concentration at maximum depth (mg/L)

Z	=	depth (cm)		
Z*	=	D/V (cm)		
V	=	advective velocity (cm/d).		
D	=	sum of dispersive process coefficients (cm ² /d)		
	= `	$D_m + \alpha \times V$		
where	:			
	D_m	= molecular diffusion coefficient (cm^2/d)		
	α	 longitudinal hydrodynamic dispersivity (cm) 		
	Z _{max}	= depth at which maximum concentration occurs (cm).		

The analytical solution of the advection-dispersion equation, in this and other forms, has been widely applied to determine diffusion coefficients, advective velocities, and fluxes in sediments (Maris and Bender, 1982; Maris et al., 1983; Matisoff, 1980; Sayles and Jenkins, 1982; Cornett et al., 1989; Anati, 1994; Lerman and Lietzke, 1977; Lerman, 1975).

A range of advective velocities was used to represent different potential flow scenarios. On the lower end, a velocity that corresponds to the sedimentation accumulation rate was used, and at the upper end, velocities were used that correspond to specific loadings of total mercury and methylmercury. Due to sediment accumulation and consolidation, a minimum upward advective velocity equal to a sediment accumulation rate of 0.83 cm/year (yr) (0.0023 cm/day) can be expected in the absence of advection caused by other forces. This value is the average of accumulation rates based on cesium-137 profiles reported from sediment cores collected by PTI for Honeywell in 1992 (0.86 and 0.86 cm/yr) and 1996 (0.72 cm/yr), and by Rowell (1992) in 1989 (0.82 and 0.88 cm/yr).

The upward velocity necessary to cause a specific mercury loading from porewater to the water column can be calculated based on the concentration of mercury in porewater and the area of the sediments. Based on data collected by Honeywell/Exponent in 2000, the average concentrations of total mercury in the top 4 cm of porewater from triplicate samples from the deep-water Stations S303 (16 m), S354 (17 m), and S355 (16 m), were 15.9, 25.8, and 22.4 ng/L, respectively, with an average of 21.4 ng/L. The average concentrations of methylmercury in the top 4 cm of porewater from triplicate samples from the gep-water from triplicate samples from the same deep-water stations were 8.73, 13.6, and 15.5 ng/L, respectively, with an average of 12.4 ng/L.

For a loading of total mercury that corresponds to the increase in mass of total mercury in the hypolimnion during the 120 days between May 25 and September 21, 1992 (about 660 g), the required flow is $2.7 \times 10^5 \text{ m}^3$ /day. Distributing this flow across the area of sediment at water depths greater than 9 m (8 × 10⁶ m²) indicates that a velocity of 3.4 cm/day is necessary to produce this loading.

For a loading of methylmercury that corresponds to the increase in mass of methylmercury in the hypolimnion during the same period (about 330 g), the required flow is 2.3×10^5 m³/day, and the necessary velocity is 3 cm/day. In addition to these values, a near-zero velocity of 10^{-6} cm/day, and an intermediate velocity of 0.02 cm/day, were used in the model.

The sum of coefficients for dispersive processes, D, is calculated with the equation given above. The molecular diffusion coefficient of chloride is temperature-dependent, and values of 0.26 cm²/d, 0.33 cm²/d at 18°C, 0.67 cm²/d at 13°C, and 0.87 cm²/d at 0°C to 1.48 cm²/d at 18°C have been reported by Lerman (1975), Matisoff (1980), Duursma (1977), and Li and Gregory (1974), respectively. Using a temperature of 7°C, and interpolating between the temperatures at which Li and Gregory (1974) measured D_m, a value of 1.1 cm²/day is assumed for the sediments. Longitudinal hydrodynamic dispersion is a function of advective velocity and the dispersivity of the porous medium. The value of the dispersivity is on the order of 1 cm (Gelhar et al., 1992). For advective velocities of 10⁻⁶, 0.0023, 0.020, 3, and 3.3 cm/day, the corresponding longitudinal dispersion coefficients ($\alpha \times V$) are 10⁻⁶, 0.0023, 0.020, 3, and 3.3 cm²/day. The sum of these values and D_m (1.1 cm²/day) were used in the model. As can be seen in Figure 6-3, hydrodynamic dispersion is negligible at all but the highest velocity tested.

The lower-boundary condition is from Effler et al. (1990), and shows a chloride concentration of 45,000 mg/L at a depth of about 532 cm. It is likely that the linear profile Effler observed extends downward and reaches a concentration equal to that of the natural brines (155,000 mg/L) in the Syracuse Formation (Kantrowitz, 1970). In the absence of that value, a lower-boundary condition of 45,000 mg/L at 532 cm was used in the model. The upper-boundary condition in 1989 was about 470 mg/L, and in 1992 was about 350 mg/L. Model results are fairly insensitive to the difference between these two values, and because Effler's sediment data set extends deeper, the value related to this data (470 mg/L) was used.

Chloride profiles measured by Effler et al. (1990) and PTI (1993d) were used for comparison to model predictions. Porewater chloride concentrations collected in the 1992 RI sampling were converted from concentrations on a dry weight (mg/kg) basis to a porewater (mg/L) basis using percent water in the equation:

Porewater Cl (mg/L) = Dry Wt Chloride (mg/kg) × ([100 percent water]/percent water)

The cores collected from the deep southern basin by Effler in 1989 and by PTI in 1992 (Station S51) were used for this evaluation. These data were used because they have the greatest spatial scale and the finest scale of resolution. One of Effler's cores was from the top 95 cm, while the other core was from the 107 to 532 cm interval. A composite profile from these two cores was used. Due to core compaction in the open-barreled corer used in 1992, deeper sediments collected by PTI show a downward-concave chloride profile. These data were not used in the comparison. Profiles from cores collected in the littoral zone of the lake were not used, because they have different patterns due to different boundary conditions and velocity, and the focus of this analysis is the profundal sediment environment.

The concentration profiles from sediment cores and the results from the model are shown in Figure 6-3. The chloride data from Effler et al. (1990) and PTI (1993d) plot on top of each other and are indistinguishable. The predicted profiles for velocities of 3 and 3.6 cm/day also plot on top of each other. Figure 6-3 shows that upward advection causes an upward bulge in the profile, and that an upward velocity of 0.0023 cm/day or more would produce a profile that is clearly inconsistent with observed linear profiles.

This confirms that the distribution of chloride in the sediments is controlled by diffusion alone. Figure 6-4 compares observed profiles to predicted profiles for velocities between -0.001 and +0.001 cm/day, and shows that a velocity between -0.0001 and +0.0001 cm/day (4 cm/100 yrs) is likely.

The linearity of the chloride profile and diffusion-dominated transport is not unique to this location in the lake. Chloride profiles from all profundal cores collected in 1992 are shown in Figure 6-5. The vast majority of these profiles are linear and show that transport in sediment porewater is controlled by diffusion. Six samples out of 42 show nonlinear profiles. Two cores (Stations S56 and S57) show similar nonlinear profiles and are only a few hundred feet apart. Field logs for these two stations indicate vertical heterogeneity in texture, which is unusual for profundal samples and may reflect the influence of adjacent Solvay Wastebeds. The variations in the other cores are less easily explained. Nonetheless, and more importantly, none of the nonlinear profiles have a shape that indicates upward advection of porewater.

Given a maximum upward velocity of 0.0001 cm/day, the volume of water entering the hypolimnion during summer stratification would be 930 m^3 (2,900 m³/yr), and the associated total mercury and methylmercury loadings would be 0.020 and 0.012 g, respectively. The maximum total mercury loading of 0.020 g from porewater advection during summer stratification is negligible, compared to the increase in total mercury mass during stratification (660 g). Similarly, the maximum methylmercury loading of 0.012 g from porewater advection is negligible compared to the increase in methylmercury mass during stratification (340 g). Thus, the simple advection of porewater does not present a significant source of mercury to the lake under an assumed absence of chemical reactions within the sediment (i.e., the sediments are inert). However, as will be discussed later in this section, this does not preclude the production of dissolved-phase mercury species at or near the sediment-water interface. Evidence suggesting such a process is presented in Section 6.1.1.5.

6.1.1.4 Diffusive Flux from Sediment Porewater

Diffusive flux is the rate at which substances are released from sediment to overlying water caused by diffusion along a concentration gradient. For purposes of this discussion, it does not include groundwaterdriven advective flux of substances from sediment to overlying water. Diffusive flux is often difficult to quantify, and previous studies have estimated flux of substances using flux chambers (e.g., Penn et al., 1994) and porewater profiles (e.g., Hurley et al., 1994). Both techniques were used in the RI. Results of the flux chamber study were highly variable and were not considered suitable for this analysis (NYSDEC/TAMS, 1998b).

The diffusive flux of total mercury and methylmercury from sediment to overlying water can be estimated from porewater data collected during Phase 2A in 2000, assuming the sediments are non-reactive. As discussed later in Section 6.1.1.5, there is strong evidence to suggest this is not the case in the hypolimnion. However, the diffusion calculation is completed here to primarily provide an estimate of this flux for epilimnetic sediments, where in situ dissolved mercury production is not evident.

In the absence of reactivity within the diffusion zone, the diffusion equation is:

$$F = \left(\frac{\varphi D_w}{\theta^2}\right) \frac{dC}{dZ}$$

where:

F	=	diffusive flux (ng/m ² -sec)
D _w	=	diffusion coefficient of the solute in water without the presence
		of the sediment matrix (m ² /sec)
dC	=	change in concentration between porewater and overlying
		water (ng/m ³)
dΖ	=	change in depth between porewater and overlying water (m).
arphi	=	sediment porosity
θ	=	tortuosity (dimensionless).

Tortuosity is a parameter that is not readily measured, but has been related to porosity by Boudreau (1996) as:

$$\theta^2 = 1 - \ln(\varphi^2)$$

The porosity of surface sediments has not been measured directly, but data from the 1992 RI sampling indicate a moisture content of 62 percent (wet weight), specific gravity of 2.5 g/cc (dry weight), and total solids of 35 percent (wet weight) for surficial sediments. A porosity of about 82 percent can be estimated from these three physical properties. The corresponding tortuosity value (θ) is 1.18.

Previous studies on patterns of total mercury in Onondaga Lake (Wang and Driscoll, 1995) suggested that the dominant species of mercury under oxic conditions in the epilimnion (i.e., in the absence of sulfides) are $HgCl_x$ and $Hg(OH)_x$ complexes, while sulfide complex forms HgS_2^{-2} and $Hg(HS)_2^0$ are dominant under anoxic conditions found in the hypolimnion. The predominance diagrams from which these complex species are derived usually do not consider organic complexation due to a paucity of thermodynamic data on mercury, and especially methylmercury, binding with polyfunctional natural ligands such as humic and fulvic acids (Ullrich et al., 2001). Mercury speciation in oxic fresh waters is largely dominated by organic mater (Lövgren and Sjöberg, 1989; Coquery et al., 1997).

The accuracy of the estimated diffusion flux depends on the choice of diffusion coefficient and the resolution of the porewater measurements. The coarse resolution of the porewater measurements in this investigation limits the accuracy of interfacial mercury gradient. Nonetheless, the results are considered sufficient to provide an order-of-magnitude estimate.

As part of this first-order estimate of diffusive flux, it was assumed that the neutrally charged species of total mercury and methylmercury exist in porewater (i.e, $HgCl_2^0$ and CH_3HgCl^0). These species were chosen as representative based on their likely presence in oxic epilimnion surface and porewater. Molecular diffusion coefficients are frequently derived as a function of molecular mass. $HgCl_2^0$ and HgS_2^{-2} have similar molecular masses (272 versus 265 g/mole). Similarly, CH_3HgCl^0 (248 g/mole) has a similar molecular mass as the CH_3HgS (251 g/mole). Thus, the molecular diffusivities derived for the chloride species can be considered representative of the sulfide species as well, in addressing diffusion under anoxic condition in the hypolimnion.

The $HgCl_2^{0}$ and CH_3HgCl^{0} species should provide an upper-bound estimate of non-reactive diffusion fluxes since they represent relatively small complexes and, thus, should have relatively high rates of diffusion. The diffusion coefficients (m²/sec) at 25°C were estimated according to Schwarzenbach et al. (1993), as:

$$D_W = \frac{2.3 \times 10^{-8}}{V^{0.71}}$$

where:

V = the liquid molar volume (cm³/mol) estimated as the ratio of molecular weight to liquid density.

The molecular mass and liquid density for $HgCl_2^{\circ}$ are 272 g and 5.4 g/cm³ and for CH_3HgCl° are 251 g and 4.1 g/cm³. The corresponding diffusion coefficients at 25°C are 1.42×10^{-9} m²/sec and 1.24×10^{-9} m²/sec, respectively. Because the sulfide species will also be of similar molecular weights as the chloride species assumed above, these values of the diffusion coefficients were also used for the anoxic hypolimnion. The average temperatures in the epilimnion and hypolimnion were 20°C and 10°C, respectively, during the stratified period.

Temperature corrections to diffusion coefficients at 25°C were made according to the relationship (Lerman, 1979):

$$D_{T1} = D_{T2} (1 + 0.048 \Delta t)$$

where:

 D_{T_i} = the diffusion coefficient at temperature T_i Δt = the temperature difference.

Diffusion rates were calculated using the Phase 2A 2000 data. The calculated diffusion rates were based on the 0 to 4 cm (dZ = 2 cm) interval and overlying water concentrations assumed to be zero for an upperbound estimate. This estimate is limited in vertical resolution due to the lack of detailed information on

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porewater concentrations near the sediment-water interface (i.e., less than 4 cm). The estimated length of the diffusional pathway has a significant impact on the magnitude of the diffusional flux. This is discussed in more detail later in Section 6.1.1.5.

Table 6-14 shows calculated diffusion rates for total mercury and methylmercury at the seven stations that were sampled in July 2000 (littoral Stations S305, S344, S402, and S405, and profundal Stations S303, S354, and S355). The porewater concentrations for each station are also presented. Calculated diffusive fluxes of total mercury from the littoral sediments were 20 (Station S305), 244 (Station S344), 7,300 (Station S402), and 26 (Station S405) ng/m²-day. Diffusive fluxes of methylmercury from the littoral sediments were 5.3 (Station S305), 36 (Station S344), 110 (Station S402), and 1.5 (Station S405) ng/m²-day.

The diffusive flux of total mercury and methylmercury from sediment into the epilimnion during May through September 1992 was calculated for the surface area of sediment contacting the epilimnion $(4 \times 10^6 \text{ m}^2)$. The period of stratification is defined as May 25 to September 21, 1992, because water column sampling inclusive of those dates indicated thermally stratified conditions. To estimate the loading of mercury to the epilimnion, the littoral zone was subdivided into four segments (see Figure 6-6) based on the location of porewater samples. Table 6-15 summarizes the four segments, the porewater stations located in each segment, and the estimated fluxes. The average mercury concentrations for the porewater stations within each segment was assumed to be representative of porewater concentrations for each segment. Because there were no porewater stations in the segment from Ninemile Creek through the northern basin to Onondaga Creek in the littoral zone, it was assumed that porewater concentrations of total and methylmercury in this segment were similar to values at Station S305. Within each segment of the littoral zone, the fluxes are assumed to occur uniformly from shore to the edge of the hypolimnion (i.e., the 9 m bathymetric contour). It was further assumed that the littoral zone has uniform width around the lake. The resulting diffusive loads of total mercury and methylmercury from littoral sediments to the epilimnion during stratification are 72 and 3 g, respectively. A discussion on the uncertainty in these loads is presented below.

Calculated fluxes of total mercury from profundal sediments (Table 6-14) were 34 (Station S303), 54 (Station S354), and 47 (Station S355) ng/m²-day, with an average of 45 ng/m²-day. Fluxes of methylmercury from the profundal sediments were 16 (Station S303), 25 (Station S354), and 28 (Station S355) ng/m²-day, with an average of 23 ng/m²-day. To estimate the diffusive loading during summer stratification these fluxes were averaged and applied across the area of profundal sediment ($8 \times 10^6 \text{ m}^2$) for the 120-day period (Table 6-15). The resulting diffusive loads of total mercury and methylmercury to the hypolimnion are 43 and 22 g, respectively.

The diffusive flux estimates derived above are based on a non-reactive sediment matrix through which diffusion takes place. Under these conditions, the flux is governed by the difference between the overlying water column concentration and the concentration at depth in the sediments (in this instance the depth is 2 cm). Based on the available data, the strictly diffusive fluxes based on these assumptions would appear to be relatively small, compared to other fluxes to the lake. However, the assumption of non-reactive sediments does not appear to be a valid one (discussed further in Section 6.1.1.5); rather, the movement

of mercury through the sediments is not governed by the difference between the two concentration horizons but by the in-situ production of dissolved mercury within the sediments. The magnitude of this production is not well known for Onondaga Lake sediments and is difficult to establish.

Similarly, the depths within the sediments where these reactions occur are also not known and may, in fact, vary temporally, possibly with the formation of the hypolimnion. Honeywell's attempts to measure this flux were largely unsuccessful (NYSDEC/TAMS, 1998b). Nonetheless, there is strong evidence for in-situ production of dissolved-phase mercury, indicating that the diffusion fluxes estimated here for the hypolimnion are clearly underestimates of total mercury transport from the sediments. In addition, it is also likely that ebullition of methane gas from the profundal sediments may significantly increase the rate of mercury transport. Further discussion of hypolimnetic mercury flux is provided below in Section 6.1.1.5. Although there is no direct evidence for in-situ production of dissolved-phase mercury in littoral sediments, it is likely that the process occurs there as well. In these littoral sediments, the presence of oxygen in the overlying epilimnetic water may limit the depth and rate of dissolved-phase mercury production. Thus, the diffusive flux estimated for littoral sediments is considered to be more representative than the hypolimnetic flux, since in-situ production may be minimal in the littoral zone, as opposed to the hypolimnetic diffusive flux, which is clearly underestimated.

6.1.1.5 Hypolimnetic Accumulation of Total Mercury: Evaluation of Potential Sources

Up to this point in the chapter, Section 6.1.1 has described the estimates of mercury loads to the lake. The following discussion examines the measured evidence for mercury input to the lake based on the increase in the hypolimnetic mercury inventory. During the period of stratification, the concentration of mercury in the hypolimnion increases roughly fourfold (see discussion in Section 6.1.2), representing an addition of approximately 660 g of mercury. This increase is relatively small in comparison to many of the ongoing fluxes to the lake, which are as much as an order-of-magnitude greater. However, this increase is unique in that it occurs solely in the hypolimnion (no similar increase is observed in the epilimnion, despite typically larger fluxes to that layer), and rapidly disappears during fall turnover.

In addition to the increase in total mercury inventory, the 1992 sediment trap data indicate that there is additional particulate mercury in the hypolimnion relative to the epilimnion. Although there is some uncertainty in the absolute difference between fluxes represented by the sediment traps, the results suggest a greater flux of particulate mercury leaving the hypolimnion than entering it from the overlying epilimnion. The net increase in the particulate mercury flux across the hypolimnion is on the order of kilograms, thus also suggesting the presence of other mercury sources to the hypolimnion.

Dissolved-Phase Mercury Production and Release from the Sediments

The calculations presented in Sections 6.1.1.3 and 6.1.1.4 assess the likely magnitude of several different mechanisms for the release of mercury from the sediments. In each instance, mercury release is contingent upon the displacement or diffusion of mercury species from the sediment to the overlying lake water. The calculations are premised on the absence of species production or loss and simply assume that mercury

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concentrations in the sediment porewater represent the nature and concentration of mercury at the release point.

A closer examination of the profundal porewater profiles (see Figure 6-7) reveals the occurrence of a significant maximum in mercury concentrations in the profundal sediments, indicating that this is not the case. This maximum value (in the 0 to 4 cm interval in all three profundal cores), along with the concentration gradients above and below this interval, can only occur via the production of dissolved mercury species at this depth. Lacking greater resolution, the actual depth of dissolved mercury production cannot be discerned, but it is clearly within the top 4 cm of the sediments. Thus, the profundal surficial sediments are clearly a zone of dissolved-phase mercury production. Factors such as the depth and thickness of the dissolved-mercury production zone cannot be discerned from the data, but will have a significant impact on the magnitude of this flux.

Also shown in Figure 6-7 are the profiles from the four littoral zone cores. While these profiles contain higher concentrations overall, there is no distinct maximum near the sediment-water interface, suggesting that diffusion may be the governing process in these sediments, unlike the hypolimnion.

The sediment concentrations measured in the upper 4 cm of the profundal cores do not represent an equilibrium concentration, but, rather, a measure of the balance between in-situ production of dissolved-phase mercury and diffusional transport at the time of sampling. Given the significant gradients to the observed concentrations above and below this layer, it is likely that higher concentrations exist within the 0 to 4 cm layer. The magnitude of the profundal sediment flux to the hypolimnion is strongly dependent on the location of the dissolved-phase mercury production layer in the sediment. As an example, the diffusion calculation presented in Section 6.1.1.4 can be modified in a simple manner to show the sensitivity of the estimate to in-situ production. If the maximum concentration occurs at the sediment-water interface (i.e., 1 mm below the surface instead of 2 cm), the flux will increase by more than an order-of-magnitude. Additionally, if the concentration maximum is simply twice that measured (the gradients to both vertically adjacent samples in each core are sufficiently steep that this is well within the range of possibility), this would serve to at least double the flux.

Comparison of total mercury and hydrogen sulfide profiles within the hypolimnion also suggest that the lake bottom is a source of mercury to the water column. Within the hypolimnion there is a distinct vertical gradient in hydrogen sulfide concentrations, with concentrations near the bottom typically greater than the concentrations near the top. Effler et al. (1996b) reported that vertical profiles of hydrogen sulfide and sulfate in the hypolimnion demonstrate that most of the sulfate reduction occurs within the sediments or at the sediment-water interface. This gives some indication that sulfides are produced in the bottom sediments and that diffusion controls distribution in the water column above the sediments. Previous studies (Wang and Driscoll, 1995) identified a strong correlation between total mercury and hydrogen sulfide in the lower waters. The production of high concentrations of sulfide in the sediments could complex with mercury and increase the concentration of mercury from the profundal sediments, and subsequently contribute to the accumulation of mercury observed in the hypolimnion of Onondaga Lake.

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The coincidence of sulfide and mercury profiles can be seen in the water column data from September 1999 (Figure 6-8 and Chapter 5, Figure 5-143). In this instance, both total mercury and sulfide show a strong gradient across the hypolimnion, consistent with a source at the lake bottom. Subsequent 1999 profiles are impacted by fall turnover and thus are not useful in this examination. Other profiles of mercury concentrations in the lake from the summer of 1992 also suggest gradients in the hypolimnion (see Chapter 5, Figure 5-142), although these results are not as distinct as the 1999 result.

Although there is clear evidence for its occurrence, there is significant uncertainty surrounding the magnitude of the production of dissolved-phase mercury species within the sediments and the subsequent release to the lake. The results of the profundal diffusive flux given in Section 6.1.1.4 suggest that profundal diffusion alone is about 16 times too small to account for the observed hypolimnetic accumulation. However, the demonstrated occurrence of dissolved-phase mercury production in the sediment reveals the diffusion estimates to be lower bounds that may significantly underestimate the actual magnitude of the sediment flux. As discussed in the next section, it appears likely that the total mercury flux out of the sediment may be enhanced by other mechanisms during the stratified period.

Release from the Settling Particles

An alternate explanation for the increased mercury concentration is that the additional mercury is the result of mercury released from falling particles, a process termed "remineralization." This mercury would be transferred from falling particles to the water column, raising water column concentrations and lowering the mass mercury on the falling particles. If this process occurs as the particles migrate through the water column, it should be observable in sediment traps deployed at the thermocline and the lake bottom. Sediment trap data were collected in 1992 to characterize net settling in the lake, and the traps were placed at the thermocline and near the lake bottom within the hypolimnion. The traps were deployed for one-month periods during the summer stratification period when little vertical mixing is present in the lake. The traps were deployed at relatively deep levels in the lake, essentially at levels where little or no sediment resuspension could occur. In this manner, the epilimnion traps (deployed at the thermocline) captured the net settling input to the hypolimnion. In a similar manner, the hypolimnion traps captured the net settling input to the sediments.

One of the principal purposes of the traps was to measure the occurrence of any mercury input to the hypolimnion via the disintegration of falling particles (i.e., remineralization). No evidence was found for the loss of mercury from suspended solids within the water column of Onondaga Lake (see Figure 6-9). In most instances, the rate of mercury transport via total suspended solids settling remained the same or increased across the hypolimnion. That is, the particle-borne mercury flux measured in the hypolimnion sediment trap was greater than or equal to the flux measured by the epilimnion trap. Based solely on the absence of a substantive decline in the mercury fluxes with depth, the premise of remineralization of falling particles within the water column is not supported.

To further explore the possibility of remineralization, Honeywell completed another study of suspended solids fluxes in 1996. In this study, a series of sediment traps were deployed just above the sediment water

interface over different lengths of time and their results compared. Specifically, one set of sediment traps was deployed over two-week intervals while the second set of traps was deployed for longer periods, typically four, six, or eight weeks. This approach was based on the following assumption: if remineralization was occurring during a particle's residence in the water column, then particles that remain in the water column for longer periods should show greater mercury loss (lower mercury levels) than particles with shorter residence times. This premise should manifest itself in the results of the sediment trap measurements in the following way: the sum of multiple two-week trap deployments for mercury (total and methylmercury) should be systematically higher than the longer deployments (e.g., four, six, or eight weeks) that cover the same interval. In other words, the longer deployments should show greater losses of mercury from the suspended matter via the hypothesized loss process of water column remineralization.

Results of the depositions of solids, total mercury and methylmercury (Table 6-16) are highly variable and do not support the operation of the hypothesized process. For the first ten weeks (June 5 to August 12), deposition from the long-term collections exceeds the summation of shorter-term collections and is, therefore, inconsistent with the remineralization process. For the last six weeks, the results are consistent with the operation of a loss process. Overall, the primary outcome of the study yields no substantive trend and suggests that the ability to measure this flux, if it exists, is limited due to the variations in the mercury deposition measurements. This further suggests that the remineralization flux, if it exists, must be smaller than the inherent variability in the measurements. More likely, the consistent load gains observed during the first ten weeks as well as the 1992 results suggest no remineralization occurs during the primary period of the hypolimnetic inventory increase. The observed load decrease across the hypolimnion observed during the later period in 1999 is partially affected by fall turnover, thus confounding the remineralization estimate for this period. Based on these observations, there is no evidence to support the occurrence of a remineralization flux.

Sediment-Water Interface Release: Ebullition of Methane

According to studies performed by Addess (1990) the profundal sediments of Onondaga Lake produce methane gas, which bubbles out of the sediments (ebullition) at an average rate of 6 mmol/m²-day. This is consistent with the results of Honeywell's geophysical report (PTI, 1992a), which indicated that the sediment in the entire profundal zone is opaque to sub-bottom profiling because of interstitial gas accumulation, and reported areas of active venting. Effler et al. (1996b) indicated that the rate of ebullition is more pronounced at times of lower hydrostatic pressure; i.e., lower water depth such as during summer months. Studies have documented that gas ebullition can affect fluxes out of the sediments in two ways: by increasing porewater exchange rates and by transporting entrained particles, as has been documented by the studies summarized below:

• Martens et al. (1980), Martens and Klump (1980) and Klump and Martens (1981) documented that the ebullition of methane gas occurred through bubble tubes and increased the transfer rate of the porewater constituents. They stated that when bubble tubes were present, molecular diffusivities of porewater constituents were higher by a factor of more than three. These studies suggest that

the increased transfer is due to increased surface area and/or an increase in the contact between the overlying water and deeper sediments.

Studies conducted by Service Environmental & Engineering (2002) on the entrainment and transport of particles by gas ebullition at the St. Louis River/Interlake/Duluth/Tar site (SLRIDT site), a Superfund site in Duluth, Minnesota, suggest an average ebullition flux rate of 2.5 mmol/m²-day, and mean total entrained material for five stations of 0.092 g/m^2 -day. Using the average surface sediment mercury concentration of about 10 mg/kg in Onondaga Lake, and the rate of particle transfer at the SLRIDT, a particulate flux of 880 g of mercury can be inferred for the stratified period of Onondaga Lake. Notably, with the higher ebullitive rates in Onondaga Lake, the profundal sediments transferred into the hypolimnion via particle entrainment of ebullitive methane gas may be higher.

The evidence from these studies on sediment-water exchanges from ebullition suggest that the profundal sediments are a likely source of mercury to the water column inventory during the stratified period. It is likely that the release of mercury by the production of dissolved-phase mercury at or near the sediment-water interface, and the enhanced porewater and particle transfer due to ebullitive methane gas, can provide a source of mercury to the hypolimnion on the order of kilograms during the stratified period.

In comparison to the other loads within the lake, the hypolimnetic inventory increase during the stratified period (660 g) is quite small, although the apparent gain in hypolimnetic particulate mercury flux from the 1992 sediment traps (about 3,200 g) is comparable to major sources such as the tributaries. The lack of evidence for particle remineralization combined with the water column and porewater profile evidence, as well as the presence of methane gas ebullition, suggest that this inventory increase is the result of mercury release close to the sediment-water interface. While the inventory increase may represent a minor role in the lake's total mercury budget, it could provide an important source of mercury to the hypolimnetic methylmercury inventory is derived from this source. This is the same period in which hypolimnetic methylmercury production is at its peak (see Section 6.1.1.6).

6.1.1.6 Methylmercury Production in the Water Column

Methylmercury production refers to the addition of a methyl group to a mercuric ion to form methylmercury. The reaction is primarily biologically mediated (Callister and Winfrey, 1986; Gilmour and Henry, 1991), although some evidence for abiotic methylation in the environment by methylcobalamin, methyltin compounds, and humic matter has been presented (Weber, 1993). The highest rates of methylation are observed in anoxic sediments near the oxic/anoxic interface in both freshwater (Rudd et al., 1983; Callister and Winfrey, 1986; Korthals and Winfrey, 1987) and estuarine (Olson and Cooper, 1976; Compeau and Bartha, 1984) environments. Methylation has also been observed in the water column of lakes (Miskimmin et al., 1992; Watras et al., 1995). The interface between oxic and anoxic waters

appears to be an important site for methylmercury production in both stratified freshwater (Watras et al., 1995) and estuarine (Mason et al., 1993) systems.

Methylmercury production in the environment is offset by the process of demethylation, whereby the methyl group is removed from methylmercury, leaving inorganic mercury. Demethylation is an enzymatic, inducible process in many microorganisms; however, the environmental significance of microbial demethylation is unclear because methylmercury concentrations in natural waters may be too low to induce the reaction (Barkay et al., 1989). Abiotic demethylation may be the dominant pathway in many waters. Sunlight-induced demethylation has been observed in lake water samples from Ontario (Sellers et al., 1996).

Net methylmercury production is quantified by measuring the increase in methylmercury concentration in water samples over time. Typically, radiolabeled mercury (²⁰³Hg) is usually added to the sample and radiolabeled methylmercury is analyzed. Methylmercury production and demethylation can be measured independently and simultaneously with radiolabels (²⁰³Hg and ¹⁴C) (Furutani and Rudd, 1980; Ramlal et al., 1986) or stable tracers (Hintelmann and Evans, 1997).

Net methylmercury production was measured twice (in 1992 and 1996) during the RI; however, only data from the hypolimnion in September 1996 are considered acceptable for this analysis (NYSDEC/TAMS, 1998b). These data are presented in Table 6-17.

The mass of methylmercury produced in the hypolimnion from May 25 through September 21, 1992 was calculated by assigning the production rate to the concentration of mercury in the volume of the hypolimnion that had DO concentrations less than 0.1 mg/L. The methylmercury production rate is the average of the rates measured at 14 m in the northern and southern basins in 1996 (1.6 percent/day). This rate was applied to the concentration of mercury that is available to be methylated, which is assumed to be the dissolved inorganic mercury (concentration of dissolved total mercury minus the concentration of dissolved methylmercury). In the calculation, the volume-weighted average concentration on a monthly basis was used. The volume was determined based on data obtained during the geophysical survey (PTI, 1992a) and DO measurements. The estimated mass of methylmercury produced in the hypolimnion during the stratification period is 230 g. Although the calculated production of methylmercury, it is likely that the estimated value is lower, as explained below:

- The sediment trap data from 1992 suggest a gain of particulate bound methylmercury of about 300 g in the hypolimnion.
- Methylation, which is thought to be biologically mediated, is very sensitive to environmental conditions, including oxygen, sulfide, oxidation reduction (redox), and pH, which vary in the hypolimnion with depth. The most prolific site for methylation is the oxic-anoxic interface. Based on the 1996 data on methylmercury production rates (Table 6-17), the sample collected from 8.6 m in the northern basin (located at the interface between oxic and anoxic water) had a methylation

rate of 4.2 percent per day, which is much higher than the 1.6 percent per day average for the 14 m depth. If this value is averaged with the other samples containing no DO, the net methylmercury production becomes 350 g.

There is further evidence in the fall 1999 turnover data that the net methylation rate is higher than the value of 1.6 percent per day used in the above calculations. On September 27, 1999, the oxic-anoxic boundary was at 9 to 11 m deep (Chapter 5, Figure 5-145), and the maximum methylmercury concentration of 12 to 14 ng/L occurs at 9 m in the southern basin and 12 m in the northern basin. There were lower concentrations deeper in the hypolimnion, with about 2 ng/L at 15 m in the southern basin and about 8 ng/L at 15 m in the northern basin. By October 15, 1999 the epilimnion has expanded and the oxic-anoxic boundary is between 13 and 16 m and, thus, the formerly hypolimnetic waters from 9 to 15 m in depth have been incorporated into the epilimnion, along with their methylmercury inventory. However, during this period, a span of only 18 days, the concentrations of methylmercury at 15 m and below have increased to about 10 to 14 ng/L. Thus, the methylmercury inventory at 15 m depth doubles in about two weeks, suggesting that the dynamic nature of this process occurs within the hypolimnion.

Gbondo-Tugbawa and Driscoll (1998) estimated net methylation of over five times greater than tributary input. Although their modeled results reported estimates on an annual basis, this methylmercury production mostly occurred in the stratified period, when anoxic conditions exist in the hypolimnion.

While the estimated methylmercury production of 230 g from the 1996 data is used in the mass balance analysis, it is important to note from the discussion above that this value is likely low. The relative importance of the in-situ production of methylmercury is discussed in Section 6.1.2.2.

6.1.1.7 Summary of Inputs

The estimated magnitude of the total mercury and methylmercury inputs to the lake during the stratified period, from the sources discussed above, are presented in Table 6-18. The table also includes an estimate of their percent contribution to total inputs. The total mercury input to the lake from sources identified in the RI/FS Work Plan (PTI, 1991c) during the period of stratification was estimated as 3,500 g. Tributaries and Metro account for about 72 percent of the total mercury input to the lake, while groundwater contributes approximately 22 percent. Tributary inputs are also broken down in Table 6-1 into the individual tributaries, where it can be seen that Ninemile Creek, which received substantial contamination from Honeywell, is the dominant tributary source of mercury, followed by Metro and Onondaga Creek. Groundwater inputs from non-Honeywell shore areas, porewater diffusion, and precipitation inputs were estimated to contribute a combined 6 percent of the total mercury to the lake. Among these secondary inputs, the contribution from porewater (representing a direct input from the sediments) is among the least well estimated and may be substantially larger than represented in the table.

For methylmercury, tributaries and groundwater account for approximately 26 and 15 percent of the loading, respectively, to Onondaga Lake (Table 6-18). Net methylmercury production (52 percent of the total input) accounts for the majority of the input to the lake. Porewater diffusion/advection, as calculated here, only represents a minor contribution (approximately 6 percent), but may be substantially larger than estimated due to the occurrence of in-situ production of dissolved-phase mercury at the sediment-water interface and enhanced transport by methane ebullition. Precipitation appears to be a negligible source of methylmercury.

6.1.2 Transport and Fate of Mercury in the Water Column

This section discusses the transport and fate of mercury after it enters the water column of the lake. "Transport" is defined here as the net movement of mercury from one place to another within the system boundaries, while "fate" is the loss of mercury from the system or storage within the system. The basis for this discussion is water column data collected in 1992, sediment trap and methylmercury production data collected in 1996, and water column data collected in 1999.

The mass of total mercury and methylmercury in the water column was calculated for each water column sampling event in 1992 and 1999. Figures 6-10 and 6-11 show the masses of total mercury and methylmercury in the epilimnion, hypolimnion, and for the whole lake for the 1992 and 1999 sampling periods. These data suggest several major events in terms of lake mercury levels, including the following:

- The occurrence of high total mercury concentrations in the spring that are likely due to runoff (April 1992).
- A rapid decrease in concentration before summer stratification (May 1992).
- Increasing concentrations during summer stratification (June to September 1992).
- Decreasing concentrations at the end of stratification (September to November 1992 and September to October 1999).
- A sharp increase and decline after fall turnover (November to December 1999).

These increases and decreases in mass are explained by evaluating the inputs of mercury to the water column and the losses of mercury from the water column. The discussion of fate in the water column focuses on the period of stratification (May 25 to September 21, 1992) for which the most complete data set exists. A mass balance for the period is calculated below using inputs from Section 6.1.1. A mass balance approach is used because it allows identification and quantification of sources and sinks.

The transport and fate of mercury in the water column and sediments depend on the forms of mercury and the processes that move those forms. As with most metals, mercury strongly associates with particles. Particle-water partition coefficients for total mercury (K_d) were calculated from the observed

concentrations of filtered and unfiltered total mercury in the water column (PTI, 1993c) and ranged from 10^4 to 10^6 L/kg, which is consistent with other studies of mercury partitioning (e.g., Hurley et al., 1994; Babiarz et al., 2001). These partition coefficients, along with concentrations of suspended solids, indicate that 70 to 90 percent of the total mercury is associated with particles. Because the settling velocity of solids is on the order of 1 m per day, and the mean water depth of the lake is roughly 9 m, the residence time of particles in the water column is on the order of one to two weeks. Because of the strong partitioning of mercury to particles, sedimentation of mercury associated with particles is the likely fate of mercury in the water column in lakes (Hurley et al., 1994; Krabbenhoft and Babiarz, 1992; Watras et al., 1994) and estuaries (Mason et al., 1993).

6.1.2.1 Losses of Mercury from Onondaga Lake

The mass balance approach for understanding the dynamics of a contaminant requires both the inputs (sources) and the losses (sinks) to be quantified. This section discusses the losses of total mercury and methylmercury from the epilimnion (above 9 m) and the hypolimnion (below 9 m) of the lake. During stratification, the wind-driven currents mix the water column in the epilimnion. The hypolimnion, however, is rather stagnant since the thermocline resists vertical mixing in the lake.

There are numerous mechanisms by which mercury can be removed from the epilimnion. The most likely losses from the epilimnion include volatilization, outflow to the Seneca River, settling of particles across the thermocline, and mixing of water (dispersion) with the hypolimnion. Other processes that are likely to be less important on a mass-balance basis include removal of fish from the lake, net settling to the shallow sediments,² and downward advection through sediments.

Because the hypolimnion is physically isolated from the shallow regions of the lake, there are fewer mechanisms by which mercury can be removed, compared to the epilimnion. The most likely losses from the hypolimnion include settling of particles to the sediment and exchange of water with the epilimnion. Other processes that are likely to be less significant on a mass-balance basis include the settling of dead fish from the water column and downward advection through sediments.

Volatilization

Volatilization represents a loss mechanism that applies exclusively to the epilimnion and is based solely on dissolved elemental mercury, since this is the only form of mercury with a significant vapor pressure. This flux was calculated using a two-film model for exchange across the water-air interface. Average monthly concentrations of elemental mercury in the top 9 m of the water column were used, along with an assumed concentration in the air. Although Bloom and Fitzgerald (1988) reported the concentration of elemental mercury in the air in Long Island of 3 ng/m³, a value of zero was used in the calculations so as to create an upper-bound estimate of loss via this mechanism.

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² Gross settling to the shallow sediments may represent a large flux, but it is likely that this flux is offset by resuspension due to wind and other shallow-water movements.

The equation for transfer is:

$$F_{v} = K_{OL} \times \left(C_{w} - C^{*}\right)$$

where:

F_{v}	=	volatil	ization flux (g/m ² -day)		
K _{OL}	=	liquid-air interface mass-transfer coefficient (m/day)			
C_w	=	concer	tration of mercury in water (g/m ³)		
C*	=	concer concer	tration of mercury in air expressed as the water tration in equilibrium with the air		
_	=	C_A/H			
where:					
	Η	=	Henry's Law constant (atm-m ³ /mol)		
	C _A	= .	concentration of mercury in air (g/m^3) .		

The liquid-air interface mass-transfer coefficient depends on temperature and other physical characteristics of the interface, and is calculated with the equation:

$$\frac{1}{K_{OL}} = \frac{1}{k_w} + \frac{RT}{Hk_g}$$

where:

=	aqueous-phase mass-transfer velocity (m/day)
=	gas-phase mass-transfer coefficient (m/day)
=	universal gas constant (8.2057 \times 10 ⁻⁵ atm-m ³ /mol K)
=	Henry's Law constant (atm-m ³ /mol)
=	absolute temperature in °K.

The gas-phase film transfer coefficient is defined as (Nazaroff and Alvarez-Cohen, 2001):

$$k_{g} = \left[\frac{D_{a}}{0.26 \ cm^{2} s^{-1}}\right]^{2/3} (7U_{10} + 11)$$

where:

$$U_{10}$$
 = wind speed at a reference height of 10 m in m/s
 D_a = molecular diffusivity of mercury in air (cm²/s)
= 1.55/(molar mass)^{0.65} (Schwarzenbach et al., 1993).

The water side gas transfer for lakes is defined as (Nazaroff and Alvarez-Cohen, 2001):

$$k_{w} = 0.18 \left[\frac{D_{w}}{2.6 \times 10^{-5} \ cm^{2} s^{-1}} \right]^{0.57} (0.0014 U_{10} + 0.014)$$

where:

$$D_w =$$
 molecular diffusivity of mercury in water (cm²/s)
= $2.7 \times 10^{-4}/(\text{molar mass})^{0.71}$ (Schwarzenbach et al., 1993).

The value determined for the liquid-air gas-transfer coefficient (K_{OL}) is 0.35 m/day. Concentrations of elemental mercury in the lake surface averaged 9.1 × 10⁻⁸ g/m³ from June through September. Daily fluxes using an air concentration of 0 ng/m³ averaged 3.19 × 10⁻⁸ g/m²-day. Net volatilization over the surface area of the lake (12 × 10⁶ m²) using an atmospheric concentration of zero was estimated as 46 g for the stratified period.

Outflow

Outflow from the lake cannot be measured directly due to the regulation of lake level by a dam on the Seneca River. To approximate the volume of outflow, the lake is assumed to be conservative with respect to water, thus the rate of outflow is assumed to be equal to the rate of inflow. The amount of mercury exiting Onondaga Lake through the outlet was calculated by summing the volume of water entering the lake each month during the stratified period and multiplying by the average epilimnetic concentration of total mercury and methylmercury for each month. Using this approach, 700 g of total mercury and 40 g of methylmercury exited Onondaga Lake through the outlet from May 25 through September 21, 1992.

The lack of a natural elevation gradient between the lake and the Seneca River was discussed in Chapter 3. As a result, backflow from the Seneca River to the lake occurs, and this flux must be accounted for to accurately determine the net flux out of the lake. The Upstate Freshwater Institute (UFI) estimated that backflow from the Seneca River represents approximately 7 percent of the annual inflow to the lake (UFI, 1992). A similar rate of backflow was determined from the data obtained for the RI (NYSDEC/TAMS, 1998b).

The average concentration of total mercury in five samples collected from the Seneca River between May and August 1992 was 3.9 ng/L. This concentration was used with a backflow rate equal to 7 percent of the water inflow from tributaries for the stratified period. Backflow from the river contributes 40 g of total mercury. For methylmercury, an average concentration of 0.09 ng/L was detected in the Seneca River in 1992, and backflow contributes 0.9 g. Both of these contributions are small, relative to the gross outflow from the lake. Combining the gross outflow and backflow estimates, the net outflow of total mercury and methylmercury are 660 g and 39 g, respectively, during the stratified period.

Particle Settling

The losses of total mercury and methylmercury from the water column via settling particles were calculated from data collected with sediment traps during 1992. Sediment traps were also used in 1996; however, these data were not used in the mass balance calculation because the mass balance was primarily based on 1992 data. Sediment traps were deployed and collected at six stations on a monthly basis from May through November in 1992. Four locations were sampled, as follows:

- The southern (Station W1) and northern (Station W2) deep basin stations, which were sampled at both the thermocline (i.e., the base of the epilimnion, referred to as the "epilimnion trap") and near the lake bottom (referred to as the "hypolimnion trap").
- Two stations about 2,000 ft (600 m) from the shore, one in front of the in-lake waste deposit (Station W15) and one in front of the Ninemile Creek delta (Station W16) (see Figure 6-12). The latter two stations were sampled only at the base of the epilimnion, as the hypolimnion does not exist at these locations.

Table 6-19 summarizes the concentrations, fluxes, and settling losses for the 1992 sediment trap data. Figure 6-9 shows the cumulative flux obtained by the deep basin epilimnetic and hypolimnetic traps (Stations W1 and W2) during Honeywell's 1992 RI. In each diagram, the epilimnetic trap represents the load of mercury leaving the epilimnion via particle settling. These traps were deployed at the bottom of the epilimnion. Since the hypolimnion traps were deployed near the lake bottom (approximately 18 m depth), they represent the particle-borne mercury flux to the bottom of the hypolimnion. Differences between the epilimnetic flux and hypolimnetic flux, as measured by the traps, are believed to be the result of processes within the hypolimnion.

In using the sediment trap results, there is an important distinction to be made concerning the deep basin traps versus the traps located closer to shore. The locations and depths of the deep basin traps were selected specifically to be able to measure net transport through the water column. This was done by placing both stations in the deep portion of the lake, where local influences would be minimized and a sample representative of the whole lake could be obtained. Additionally, the traps were both placed so as to ensure that the particles captured had no chance of being resuspended (i.e., the particles were deep enough within the lake that wind and tributary flow would be unlikely to remobilize the particles).

This is in contrast to the traps at Stations W15 and W16, which were specifically located in regions of likely sources (i.e., the Ninemile Creek delta and the Honeywell shoreline area). In these locations, local influences are likely to create much higher deposition rates. The proximity of these traps to the edge of the profundal zone may indicate a significant particle deposition rate to the hypolimnion that is not reflected in the deep basin stations. However, it is likely that these are localized effects and there are other regions, such as the northeastern rim of the lake, wherein deposition may be less than that observed in the deep basins due to the lack of particle sources. Such horizontal differences are expected, given lateral sediment

transport, biological activity, and resuspension in the littoral zone (Wieland et al., 2001; Sarin et al., 2000; Bloesh and Uehlinger, 1986).

In Figure 6-9, the southern basin shows a net increase mercury flux across the hypolimnion for the entire period of study, whereas the northern basin shows a net gain throughout the stratified period, until October, when a marked change in loading takes place at turnover and the particles appear to have a net loss to the hypolimnion. As shown in Table 6-19, mercury fluxes in the hypolimnetic sediments traps were consistently greater than the epilimnetic traps during the stratified period (see Figure 6-9). However, the magnitude of the difference between the two sets of traps is relatively small, representing about 30 percent of the hypolimnion trap results. While this difference suggests a load gain of mercury across the hypolimnion, there are many uncertainties in estimating the magnitude of this gain. In addition to the results for the deep basins, results were obtained for the other two traps (Stations W15 and W16) deployed closer to shore near the edge of the littoral zone in 1992. In both of these stations, the particle fluxes at the bottom of the epilimnion were substantially higher than those measured in the deep basin stations, regardless of depth (see Table 6-19).

Besides the changes in sediment trap mercury fluxes, there are large changes in the particle-borne methylmercury flux relative to total mercury. For example, in the July sample pairs for the deep basins, the ratio (0.05) of the methylmercury flux to the total mercury flux at the bottom of the hypolimnion is more than twice that observed for all of the epilimnetic traps (0.02). This result is consistently observed in each deep basin pair (see Figure 6-13). Notably, the two stations closer to shore have an almost constant ratio of 0.02 throughout the investigation (except for November) while the epilimnetic ratios at the deep basin stations vary during the year, although the values are nearly always less than or equal to the paired hypolimnetic ratio (August in the southern deep basin is the one exception to this).

This data set is not considered sufficient to completely characterize the net results of mercury-related reactions within the hypolimnion. This issue is beyond the objectives of the original sampling program.³ However, the data do suggest that the materials which fall from the epilimnion are modified as a result of their passage through the hypolimnion. Based on the deep basin results, both total mercury and methylmercury fluxes increase, with a measurable change in the proportion of methylmercury to total mercury, during most months of the stratified period. More significantly, the ratio of methylmercury to total mercury observed in the hypolimnion was distinctly higher than that observed in the stations closer to shore, indicating that the particles trapped in the nearshore traps were not the same as those in the hypolimnion, again suggesting alteration within the hypolimnion.

In summary, the sediment trap data indicate that the downward flux of mercury associated with settling particles is not uniform across the epilimnion, but rather that there are local sources that can have impacts at least 2,000 ft (600 m) out into the lake. In contrast, particle settling in both deep basins is relatively consistent at each depth, with higher mercury-settling fluxes observed at the lake bottom. As the deep basin

³ The 1992 sediment trap program was intended to characterize the scale of the particle-borne mercury fluxes in the lake. As implemented, the 1992 program did provide useful information toward this objective.
traps are least likely to be affected by littoral zone influences, their fluxes were used to estimate "typical" mercury fluxes in Onondaga Lake. The total mercury and methylmercury loads via settling particles from the epilimnion and the hypolimnion were calculated by multiplying the mercury flux rate, the number of days, and the horizontal area of the thermocline (Table 6-19). The epilimnetic loads for the stratified period were estimated as 7,500 grams of total mercury and 250 grams of methylmercury. The hypolimnetic loads for the stratified period were estimated to be about 11,000 grams of total mercury and 560 grams of methylmercury.

Dispersion

Hydrodynamic dispersion exchanges water and associated solutes across the thermocline due to windgenerated turbulence in the epilimnion. Mathematically, vertical dispersion across the thermocline is the same as molecular diffusion. The flux across the thermocline depends on the concentration difference between the epilimnion and the hypolimnion, and a mixing coefficient. The equation used to calculate vertical dispersion is:

$$J_{d} = D_{v} \times (C_{e} - C_{h})$$

where:

J _d	=	dispersive flux (ng/m ² -d)
D _v		vertical dispersion coefficient (m/d)
Ce	=	concentration in epilimnion (ng/m ³)
C_h	-	concentration in hypolimnion (ng/m ³).

The vertical dispersion coefficient is commonly determined by performing a thermal balance on the hypolimnion. Effler et al. (1996c) estimated vertical mixing rates from 0.01 to 0.1 m/day for the stratified period. The volume-averaged concentrations for the epilimnion and hypolimnion were calculated for days when sampling occurred and were interpolated between them. The daily mass exchanged was determined by multiplying the daily flux by the area of the thermocline ($8 \times 10^6 \text{ m}^2$), and the total flux was the sum of daily fluxes between May 25 and September 21, 1992. Using the average vertical mixing rate, the mass of total mercury and methylmercury transferred from the hypolimnion to the epilimnion during this period is estimated to be 140 and 110 g, respectively.

6.1.2.2 Mercury Fate During Stratification

The total mercury and methylmercury inputs from Section 6.1.1 were combined with the losses discussed in Section 6.1.2.1 to calculate the mass balance during summer stratification. Mass balances were calculated for Onondaga Lake as a whole and for the epilimnion and hypolimnion individually.

Total Mercury During Stratification

Based on the sources that had been originally identified in the RI/FS Work Plan (i.e., tributaries, groundwater, porewater diffusion and advection, and precipitation), an estimated 3,500 g of total mercury was input to the lake, on a whole-lake basis, from May 25 to September 21, 1992. About 72 percent of the estimated total mercury inputs originated from tributaries and Metro, while groundwater contributed an estimated 22 percent. During this period, the mass of total mercury in the lake's water column increased from 640 to 1,500 g, a gain of 860 g, more than doubling the original May 25 inventory. Table 6-20 summarizes the estimated initial conditions, sources, fate, and final conditions for total mercury for the period of summer stratification. While many of the fluxes are relatively well known, the mass balance cannot be closed based on the sources originally identified in the RI/FS Work Plan (PTI, 1991c). Specifically, the whole-lake mass-balance calculations yield a discrepancy of 8,800 g of total mercury loss from the lake that is not accounted for in the lake inputs identified in the RI/FS Work Plan. These results suggest the existence of an additional source(s) of total mercury whose contribution to the lake may be equivalent to or greater than the sum of all external inputs to the lake identified in the RI/FS Work Plan. These sources are identified in Sections 6.1.1.5 and 6.1.3, and likely provide the basis to close the gap in the mercury budget.

The sources, fates, and initial and final conditions for total mercury in the epilimnion and hypolimnion regions are summarized in Tables 6-21 and 6-22, respectively. Because the lake is segmented in this analysis, some external transport processes that affect only one lake region (e.g., volatilization from the epilimnion) are not relevant for the other lake region and are not included, while some internal transport processes (e.g., dispersion across the thermocline) that do not affect the lake as a whole become relevant and are included.

In the epilimnion, the sources contributed on the order of 3,600 g of total mercury, while about 8,000 g is removed via settling, outflow, and volatilization, resulting in a discrepancy of about 4,400 g. Thus, a significant source(s) in addition to those identified in the RI/FS Work Plan, is needed to complete the mass balance calculation. The likely additional source (resuspension of the Honeywell in-lake waste deposit) is discussed in Section 6.1.3.

The 1992 sediment trap data indicate significant horizontal differences in sedimentation rates between the nearshore sediment traps and the deep basin traps. Several studies have suggested that such horizontal sediment trap differences may be due to resuspension caused by high wind or turbulent conditions (e.g., Wieland et al., 2001; Eadie et al., 1984, 1994; Bloesh and Uehlinger, 1986; Robbins and Eadie, 1991). Alternatively, the higher nearshore sedimentation may be due to biological activity in the littoral zone. Notably, the two nearshore littoral zone traps were placed close to two of the most contaminated areas of the lake: the Honeywell shoreline area and the Ninemile Creek delta. The distribution of mercury in sediments indicates that some of the highest mercury concentrations are found in the Honeywell in-lake waste deposit of the Honeywell shoreline area (Chapter 5, Figure 5-2). The role of this in-lake waste deposit material as a possible additional source in explaining the discrepancy in the epilimnion mass balance is evaluated in Section 6.1.3.

In the hypolimnion, the largest input of mercury (7,300 g) is via particles settling through the thermocline from the epilimnion, entering the hypolimnion at its upper boundary. In a similar manner, the settling of particles to the sediments at the bottom of the hypolimnion of about 11,000 g is the largest output for this layer. The difference between these two fluxes suggests a net loss of mercury from the hypolimnion due to settling, as discussed previously. Given the uncertainties in the values, the exact magnitude of this flux is not considered well defined, but it would appear to be on the order of several thousand grams during the period of stratification.

During the stratified period, while the epilimnion concentration of total mercury is about 5 ng/L, the concentrations in the hypolimnion build from 5 ng/L to about 25 ng/L, for a total accumulation of between 600 and 700 g. This mercury mass has a greater proportion of dissolved-phase mercury than observed in the epilimnion. Specifically, based on the 1992 data, about 50 percent of the hypolimnetic mercury was dissolved, and based on the 1999 data, nearly 100 percent was dissolved. As discussed above and in Section 6.1.2.1, evidence from sediment trap studies in 1992 and 1996 suggest that the falling particles alone cannot explain this increase in total mercury in the hypolimnion (i.e., there is no evidence for mercury remineralization). Although the source of this buildup of mercury in the hypolimnion is unclear, it may play an important role in the methylmercury budget. It appears that the profundal surficial sediments are responsible for this flux, and although the absolute magnitude of the flux cannot be well estimated from the available data, it would appear to lie between the net gain observed in the hypolimnion water column (660 g) and the sum of this hypolimnion.

Overall, the total mercury mass balance is relatively poorly constrained for the stratified period, based on the large imbalance between inputs and outputs. Resolving some of the uncertainty in fluxes, such as the particle sedimentation rates, may serve to improve the balance. However, the imbalance is so large that it is unlikely that it stems solely from uncertainties in the fluxes identified in the RI/FS Work Plan. It is more likely that additional fluxes, such as sediment resuspension and mercury release at the sediment-water interface, constitute the additional inputs. Of these, resuspension is probably the larger and impacts the epilimnion most directly. Mercury releases from the sediments enhanced by methane gas ebullition and dissolved-phase mercury production are largely limited to the anoxic hypolimnion. This noted, it is the latter flux which would appear to more directly influence the rate of methylation within the lake waters.

Methylmercury During Stratification

A similar analysis for methylmercury shows a very different distribution of sources and fates, compared to total mercury. On a whole-lake basis, it is estimated that inputs of methylmercury totaled about 440 g. Of this, internal generation of methylmercury was the dominant source, contributing at least 52 percent of the total inputs. Tributaries and Metro combined contributed about 26 percent, with groundwater estimated to contribute about 15 percent and porewater diffusion about 6 percent. Of the total output of about 660 g, about 560 g are due to settling (85 percent), 60 g are lost to demethylation within the epilimnion (9 percent), and 39 g are lost through the lake outlet (6 percent).

Ignoring the fact that methylmercury production is likely underestimated in the mass balance, these estimates would suggest that inputs and outputs are nearly balanced. However, during the stratified period, the mass of methylmercury in the water column increased from 62 to 380 g, which is inconsistent with a true mass balance and further supports the assertion that in situ methylmercury production is underestimated. Table 6-23 summarizes initial conditions, sources, fate, and final conditions for methylmercury for the period of summer stratification. The buildup of the in-lake inventory (318 g) represents a significant mass of methylmercury that is unaccounted for. This inventory increase is about 150 percent of the estimated external inputs to the lake.

Like the total mercury balance, the methylmercury budget has a very large fraction that is unaccounted for. Unlike the total mercury budget, the imbalance in methylmercury is based largely on the change in the lake inventory. Uncertainties in the rates of methylation and particle setting are possible sources for this imbalance, since only these processes have sufficient magnitude to affect the balance at a meaningful level. Higher methylation rates or less loss via particles could both serve to bring the mass balance into better agreement. The sources, fates, and initial and final conditions for methylmercury in the epilimnion and hypolimnion are summarized in Tables 6-24 and 6-25, respectively. Uncertainties in particle settling are also likely concerns for a total mercury budget where outputs from the lake are substantially larger than the inputs. In the latter instance, however, the change in the lake inventory is small, relative to the particle settling fluxes.

For the epilimnion, the mass balance for methylmercury is better constrained, compared to the hypolimnion balance, with the scale of the imbalance being about 46 percent of the total inputs. The balance of input and loss processes in the epilimnion serve to keep the methylmercury concentration to less than 1 ng/L, most of which is associated with particulates.

For methylmercury in the hypolimnion, the mass balance is not well constrained, with the scale of the imbalance being nearly equal to the sum of all estimated inputs for the stratified period. Uncertainties in methylmercury production, particle settling, or release from the sediments affect this mass balance, since these processes are themselves relatively poorly constrained. Nonetheless, the major fluxes governing methylmercury concentration in the layer have probably all been identified in this mass balance, which distinguishes it from the total mercury mass balance calculations which has sources in addition to those identified in the RI/FS Work Plan. As noted in the mass balance, a relatively small proportion of the methylmercury budget is contributed from external sources. The pattern of methylmercury concentrations suggests that the bulk of the methylation is taking place at a discrete depth in the water column, with maximum production occurring close to the oxic/anoxic boundary. The concentrations of methylmercury in the hypolimnion build to a maximum of about 14 ng/L, which is either 50 percent (based on the 1992 data) or nearly 100 percent (based on the 1999 data) in the dissolved phase.

Methylmercury in Fish

There is an additional fate for methylmercury that is not critical to the mass balance but is important for the biological impacts of the contamination. Methylmercury is the principal form of mercury found in fish and

other animals. Most of the biological sampling for mercury in Onondaga Lake has been for fish. Several potential exposure routes for fish are as follows:

- Exposure to the low concentrations of dissolved methylmercury in the epilimnion.
- Exposure to more elevated concentrations at the thermocline.
- Exposure to more elevated concentrations for the period during and after fall turnover (approximately two months). Note that many fish migrate out of the lake at this time due to increased ammonia and other factors.
- Consumption of benthic invertebrates in the littoral zone of the in-lake waste deposit or from littoral zone sediments elsewhere in the lake, nearly all of which contain some degree of mercury contamination.
- Consumption of zooplankton, which typically have diurnal vertical migration and may enter the thermocline, where they may accumulate elevated concentrations of methylmercury.
- Consumption of detrital-feeding zooplankton that may methylate mercury in their digestive tracts.

Any or all of these routes of exposure may play a role in regulating mercury concentrations in Onondaga Lake fish. However, some insight into mercury exposure can be gained by looking at the relative amounts of mercury in the fish from the 1992 collections in regards to feeding environment, species, and species niche. While fish were collected from a series of locations around the lake in 1992 (see Chapter 2, Figure 2-13), three of these stations (see Figure 6-14) comprised the vast majority of the data:

- Honeywell lakeshore area (Station F30).
- Vicinity of the Ley Creek outlet (Station F28).
- Vicinity of the lake outlet (Station F25).

While these locations had very different mercury concentrations in their sediments and differed in their proximity to sources of mercury, the mercury concentrations in fish fillets collected from these sites did not (see Table 6-26). This could reflect a lack of fidelity to any one location in the lake, or may reflect aspects of the routes of exposure.

6.1.2.3 Mercury Fate During Fall Turnover

Fall turnover represents an important period in the lake's geochemistry. The cool, windy days of fall deeply stir the lake's surface water, eroding the thermal stratification and releasing the hypolimnetic waters from their summer isolation. With this release also comes the potential release of various reduced chemical

species whose concentrations have built up during the period of stratification. Of particular importance to this analysis is that the fall turnover has the potential to release the relatively large inventories of methylmercury and total mercury that have developed in the hypolimnion during stratification. This pathway presents a potential release mechanism for mercury present in the pelagic sediments of the lake. To the extent that the increased hypolimnetic mercury inventory was derived from the sediments (see Sections 6.1.1.4 and 6.1.1.5 for a discussion of the releases from the sediments), fall turnover serves to partially undo the sequestering of mercury that results from sediment deposition.

Potentially more important for biological and human exposure, fall turnover can also release the large inventory of methylmercury that develops during the period of stratification, potentially exposing lake biota to high levels. For these reasons, two studies of lake conditions during fall turnover were undertaken, one in 1992 and a second in 1999. Of the two, the 1999 study was much more detailed and is the primary focus of the discussion below. With respect to available level of information, the 1992 study had only monthly measures of mercury and other parameters during fall turnover (September to November), while the 1999 study had twice weekly to almost daily measurement of temperature and DO profiles for the lake, coupled with five sets of analytical profiles spaced roughly every two weeks throughout the same study period. A summary of the analysis of the fall turnover data is provided below.

In contrast to discussions of summer stratification for which the epilimnion and hypolimnion were separated by the thermocline at a 9 m depth, the thermocline is a moving boundary in the fall. Therefore, the volumes of the epilimnion and hypolimnion increase and decrease, respectively, during turnover. For the discussion that follows, the 9 m depth horizon, rather than the strict thermocline horizon, is used as a divider to avoid the illusion of mass loss or gain in the lake simply by the transfer of water. As noted later, only that mercury mass which is able to pass through the 9 m depth horizon effectively escapes from the hypolimnion or the hypolimnetic sediments.

In 1992, the thermocline began dropping in mid-September, and by the end of October the water column was completely mixed. In 1999, the water column became isothermal between October 15 and 25. Figures 6-15 and 6-16 show the changes in masses of total mercury during turnover in 1992 and 1999, respectively. Both years have the same masses of total mercury in the lake at the end of September (1,500 g). They also both show a nearly identical mass of total mercury at the first sampling when the lake is completely mixed (890 g on November 16,1992 and 850 g on October 25,1999). In 1992, the decrease in mass to this point in the fall turnover period was 41 percent, and in 1999 the decrease was 42 percent. Similar parallel trends can be observed for the methylmercury inventory during this period. Both the October and November inventories and distributions within the lake are similar in 1992 and 1999 (see Figure 6-11). The degree of agreement between the two sampling events in both the absolute levels of mercury observed and the fraction lost suggests that the conditions observed during these events occur regularly; thus, the conclusions drawn here about the behavior of mercury during this time of the year can be expected to apply to fall turnover in general.

Total Mercury

In a closer examination of the 1999 results, the detailed total mercury profiles show a decline in the mass of mercury in the lake waters, correlating to a large degree with the loss of anoxic water. Mercury concentrations above 9 m rise during this time, but quickly return to the levels seen at the end of the summer stratification period. It should be noted that the distribution of mercury in the upper, oxic zone of the lake remains principally particle-bound, despite the addition of what was primarily dissolved mercury from deeper waters (see Figure 6-17). More importantly, the decline in mercury inventory apparently occurs in association with the addition of oxygen to the hypolimnetic waters and the associated precipitation of reduced iron and conversion of sulfide to sulfate. This can be seen by reviewing Figures 6-18 through 6-20, which show the mercury, iron, and backscatterance results and Figure 6-8, which shows sulfide results, during this period.

The behavior of total mercury during this period closely mimics that of iron. As oxygen penetrates the lake, nearly all iron (80 percent) and much of the mercury (40 percent) are removed from the water column, but apparently at just the oxic-anoxic boundary. Precipitation and deposition seems the likely route, with the possibility that the formation and precipitation of amorphous iron hydroxide (Fe⁺³) from the dissolved iron (Fe⁺²) serves to remove much of the mercury from the water column as well. Indeed, for every gram of mercury that was removed by precipitation, over 6,000 grams of iron were also removed. A precipitation mechanism is further supported by the descent and increase of the backscatterance maximum during this period (see Figures 6-21 and 6-22).

It is important to note that the mercury removal process returns the water column mercury concentrations to those found in the overlying oxic waters. Regardless of the exact mechanism, it seems clear that the vast majority of the decline in mercury inventory occurs as deposition to the pelagic sediments. Little of the 600 g lost from the hypolimnion during fall turnover appears in the oxic waters of the lake. Overall, this period was characterized by a major loss of mercury from the region below 9 m, with most of the inventory being returned to the pelagic sediments. Only a small portion (17 percent) of the mercury loss from this region escapes to the region above 9 m.

A second and somewhat unexpected mercury release event occurred in 1999 after the fall turnover was essentially complete and the lake was isothermal. Between the October 25 and November 9 sampling events, a large release of mercury took place, with the lake inventory reaching the same level as was seen at the end of summer stratification period (see Figure 6-10). This time, however, the inventory increase occurred within two weeks, as opposed to the hypolimnetic inventory increase which took all summer. The October to November increase in inventory was reflected by a near-doubling of the lake concentrations at all depths in the lake (nominally, from 6 to 11 ng/L), and was not restricted to a limited region of the lake. The source of this mercury inventory increase is unknown. The inventory increase appeared to be rapidly lost, since the lake inventory declined by a similar amount by the next sampling event (December 2).

The lakewide average increase of about 80 percent appears entirely as particulate material, since the dissolved mercury concentration remained constant (see Figure 6-23). Despite the large increase in

particulate mercury, there was no corresponding increase in TSS. In fact, the TSS in both layers of the lake decreased between October 25 and November 9, reaching the lowest value seen during the entire study period (see Figure 6-24). In contrast, the backscatterance levels in the lake increase slightly everywhere, indicating a greater lakewide concentration of fine particles (see Figures 6-21 and 6-22). However, the increasing backscatterance levels continue despite the subsequent decline in mercury water column concentration. Based on these data, the source of the increased mercury concentration is unclear.

One suggestion of a possible source for the October to November increase can be obtained from the 1999 water column profiles and nearshore water column data. Data collected during the end of the summer stratification period (September 27) documented elevated levels of mercury in both the nearshore and southern deep basin surface waters (0 m) relative to other areas of the lake. The pattern of concentration suggests localized inputs of mercury to the epilimnion. (A local source comprised of the in-lake waste deposit is extensively examined in Section 6.1.3.) Lake mercury levels in September show that the epilimnion was not homogeneous either horizontally or with depth (vertically). These data raise the possibility of a sporadic southern basin source of sufficient magnitude to potentially cause some of the increased load observed in the November 9 profile.

Presumably, a lakewide re-release of mercury, by whatever means, would contaminate both basins virtually equally, while a point discharge to the southern basin would not. The magnitude and vertical extent of the inventory increase (all depths increase to about 11 ng/L) strongly suggests a lake-sediment-derived source, since this is the only known reservoir with sufficient inventory and spatial extent to affect such a change on what appears to be a lakewide basis. Resuspension of the in-lake waste deposit would also be consistent with the scale of this release.

Notably, the southern deep basin epilimnetic concentrations of mercury attained a value double the typical epilimnetic value during this release event (11 versus 6 ng/L). Since the epilimnetic water also represents the water leaving the lake at its outlet to the Seneca River, the load to the river effectively doubled during this event.

Methylmercury

The 1999 fall turnover (September 27 to October 25) serves to deliver a substantial portion of the hypolimnetic methylmercury inventory to the epilimnion, the oxic region of the lake. In part, this occurs because the removal/destruction rate for methylmercury is sufficiently slow that the methylmercury is mixed upward before it can be destroyed. This should be contrasted with the total mercury, sulfide, and iron inventories, which are largely prevented from affecting the region above 9 m by reactions that occur at or near the oxic-anoxic boundary. Only manganese is able to migrate upward at a scale similar to methylmercury.

Although the increased DO levels throughout the lake serve to curtail the production of methylmercury in the water column, the inventory that has built up during summer stratification is not so easily dispelled. During turnover, methylmercury, unlike total mercury, is able to escape the anoxic region of the lake.

Turnover serves to raise methylmercury concentrations in the top 6 m of the lake more than threefold (see Chapter 5, Figure 5-145). During the turnover period, the methylmercury inventory of the lake declines by only 35 percent. However, the inventory above 9 m increases more than 60 percent.

Interestingly, the fraction of dissolved methylmercury changes as a result of turnover, even within the oxic region of the lake. Initially, the dissolved fraction is about 100 percent in the anoxic region and about 65 percent in the oxic region. After turnover is complete, the ratio throughout the lake is about 42 percent dissolved, indicating that the liberated methylmercury from the hypolimnion is partially absorbed on suspended solids as it is mixed into the oxic waters of the lake. This can be seen by comparing the dissolved and total methylmercury inventories presented in Figure 6-11.

The region below 9 m is subject to a considerable loss of inventory during this period. This is documented in the diagrams of Figure 6-11, which shows both a rapid decline and a change in the methylmercury distribution. As the region below 9 m becomes more oxygenated and mixed with overlying water, the distribution and concentrations of methylmercury converge to a single, common condition. This is a combination of mixing and mass loss. Loss of methylmercury during this four-week period (September 27 to October 25) accounts for only 35 percent of the inventory measured at the end of the summer stratification period. Based on a mass balance calculation for the epilimnion during this period, approximately 280 g of methylmercury are added to the region above 9 m by upward mixing of hypolimnion waters. This is equivalent to about two-thirds of the 400 g inventory of methylmercury present below the 9 m boundary at the start of fall turnover (see Table 6-27). A discussion of a mass balance for the lake is presented below.

Fall turnover also has an important impact on the region of methylmercury production in the lake. In the September 27 profile, the methylmercury maximum is located at the oxic-anoxic boundary near the bottom of the thermocline. Concentrations at this depth are substantially higher than those found in waters above and below. Note that between September 27 and October 15, the depth of this maximum value increases significantly, from the 10 to 12 m interval to the 16 to 18 m interval (see the total methylmercury profiles in Chapter 5, Figure 5-145). This represents a substantial increase in the methylmercury concentrations at these depths. These observations suggest that the location of the peak layer, representing the maximum rate of methylation in the water column, can move vertically in response to lake conditions. It would appear that the methylation process is closely tied to the oxic-anoxic boundary and can move with it as the depth of the boundary varies in the lake. If the depth at which methylation occurred was fixed, then there should have been no effect on the methylmercury concentrations in the deeper lake waters as the turnover progressed. That is, when the layer of maximum methylmercury production was mixed upward into the deepening epilimnion, the methylmercury concentrations in the deeper layers of the hypolimnion should have remained unchanged. Instead, concentrations in these layers began to increase, as if the methylmercury production layer had descended further in the lake.

The methylmercury inventory and concentrations of the lake decline in a rather unremarkable way during the last three 1999 sampling events. The water column remains vertically homogeneous and oxic everywhere during this period. It is of note that there is no apparent effect from the wind event in early

November that affected the total mercury inventory so dramatically, nor is there an impact from the flow event in late November. Figure 6-11 shows the decline in inventory during this period. At the end of the entire study period, roughly 70 percent of the initial September 27 inventory remains in the lake. Approximately half of the decline (15 percent) occurs during the last three sampling events. However, concentrations above 6 m remain elevated by about 35 percent, as shown in Figure 5-145. Additionally, the dissolved methylmercury concentration at the end of the study period is five times greater than the initial concentration. Thus, this period can be best characterized as showing a gradual loss of methylmercury from the lake over time, presumably via demethylation, particle settling, and discharge. More importantly, methylmercury concentrations remain elevated in the top 6 m of the lake for at least six weeks after fall turnover as a result of the release from the region below 9 m.

Mass Balance Considerations

The fall turnover sampling event of 1999 was examined as a possible basis for estimating a mass balance for the lake over this period for mass balance estimates. While there are several significant data limitations for this period, some of them can be overcome by simplifying assumptions or the use of historical data.

Mercury

The construction of a mass balance for mercury was not considered necessary or useful for this period due to the relatively simple set of observations and the data limitations. It is apparent from the 1999 data presented (see Figure 6-16), that the lake loses a substantial mass of mercury during the fall turnover. Based on the evidence presented above, it appears that nearly all of this loss occurs within the anoxic waters. Thus, assuming that most of the other external and internal fluxes are largely unchanged during this period, the total mercury inventory loss for 1999 consists of 620 g (September 27 to October 25) via deposition to the sediments from the hypolimnion. The subsequent gain of 700 g and loss of 560 g (October 25 to December 2) cannot be readily attributed to any known flux, but the sediments of the lake are a likely candidate.

Methylmercury

Methylmercury, unlike total mercury, is more controlled by internal fluxes than external loads. Thus, a mass balance for this constituent was more valuable for understanding the processes involved. Table 6-27 was constructed using both 1999 and historical data to estimate a methylmercury mass balance for the region above 9 m. This region is the focus since it is most easily understood during this period and it is the zone of most biological exposure.

Tributary loads were estimated using 1999 hydrological data and the flow-to-methylmercury relationships developed for the 1992 investigation. While there are significant uncertainties in these values, the contribution from all tributaries is only 34 g, representing less than 5 percent of the gross fluxes in the lake.

Advective exchange from the hypolimnion was one of the most significant fluxes to the region above 9 m. This flux was estimated by assuming that the waters above and below 9 m were conservatively mixed prior to any internal reactions, such as demethylation. Thus, the flux is simply the mass transferred from the hypolimnion by homogenization of the lake water. Based on the profiles of October 15 and October 25, the lake was homogenized to a depth of 15 m and to the lake bottom, respectively. Thus, the hypolimnetic transfer ends on October 25. This advective transfer was estimated at about 260 g for the period of study.

Since the region above 9 m is entirely oxic during the study, there is no water column production of methylmercury. Thus, tributary inputs and advection from the hypolimnion represent the only fluxes that can be directly estimated. As will be shown later, a resuspension flux can be inferred from the mass balance.

The loss of methylmercury from the water column via particle settling was calculated from data collected with sediment traps during 1992 and 1996. To estimate the settling loss to the sediments, the fluxes of methylmercury that were measured in traps at the lake bottom were multiplied by the total area of the lake, to account for both littoral and profundal deposition $(12 \times 10^6 \text{ m}^2)$. During the period of turnover (September 23 to November 24, 1992) the average flux of methylmercury was 0.64 g/m²-day. During a shorter period of turnover in 1996 (September 23 to October 21), the average flux of methylmercury was 0.32 g/m²-day. These two flux estimates result in losses of methylmercury via particle settling of 500 g and 250 g, respectively, for the 1999 study period (September 27 to December 2).

These results represent a wide range of uncertainty, which impacts the mass balance estimates. Nonetheless, the range is not so great so as to make the calculation useless. Note that this flux effectively applies to the whole lake and not just the region above 9 m since it is based on a per-unit-area basis. This assumes that no additional particles are produced in the region below 9 m. Hence, this is a lower-bound estimate for particle loss for methylmercury from the lake as a whole.

It is informative to look at the fluxes for the same time period in both years. For the period between the third week in September and the third week in October in both 1992 and 1996, the fluxes of total mercury were 10.1 and 9.9 g/m²-day, respectively, and the fluxes of methylmercury were 0.40 and 0.32 g/m^2 -day, respectively. This suggests that the losses by sedimentation are fairly uniform from year to year. This observation supports the use of historical estimates of sedimentation losses for the 1999 water column monitoring period, when sediment traps were not used. In brief, the data present a range of values, but it would appear that the 1992 particle loss rate (September 23 to November 24) is most applicable to the 1999 period of study (September 27 to December 2).

The amount of mercury exiting Onondaga Lake through the lake outlet was calculated by summing the volume of water entering the lake each day from all tributaries during the time period and multiplying by the average northern deep basin (0 to 3 m) concentration for methylmercury for each day. Using this approach, it is estimated that about 30 g of methylmercury exited Onondaga Lake through the lake outlet between September 27 and December 2, 1999.

The process of demethylation is an important one for methylmercury in oxic waters. This loss was estimated from literature values (Verta et al., 1994) as 1.6 percent per day, as was discussed previously in this section. This value was applied to the volume-weighted average concentration for the region above 9 m for this calculation, which yielded a loss of 260 g of methylmercury for the study period.

The calculations presented above represent the directly estimatable fluxes used in the mass balance. In addition to these inputs and outputs, the methylmercury inventory of the region above 9 m decreased during the study period from 140 to 90 g, a loss of 50 g for the period. Assembling these results into the mass balance leaves an imbalance between 200 and 460 g for the period, depending on the assumed rate of particle deposition (see Table 6-27). That is, losses from the region above 9 m (540 to 800 g) exceeded the sum of the inputs to the region (290 g) plus the decrease in inventory (50 g).

This calculation suggests there is a significant flux of methylmercury to the region above 9 m that is unquantified. The likely candidate for this flux is the resuspension of lake sediments from the littoral zone of the lake. Over the period of study this flux would have to yield between 200 and 460 g of methylmercury, or about 3 to 7 g/day. Applying this flux over the area of the littoral zone yields a resuspension flux of 0.8 to $1.7 \,\mu$ g/m²-day. Assuming this flux is accompanied by a total mercury flux and a methylmercury to total mercury ratio in the sediments of 1 to 10, this suggests a resuspension flux of total mercury of 8 to $17 \,\mu$ g/m²-day, or 30 to 70 g/day, for the entire littoral zone. These values are quite comparable to the resuspension flux estimate for the in-lake waste deposit of 170 g/day derived later in this report in Section 6.1.3.

Summary of Fate During Turnover

Mercury

Based on the change in total mercury concentrations in the water column during the fall of 1999, the mass decreased 500 g, most of it from the lake's hypolimnion. Little of the hypolimnetic inventory of total mercury escapes to oxic waters. Thus, the combination of the hypolimnetic inventory increase combined with the fall turnover does not provide a means for total mercury to permanently escape the lake sediments. Rather, the hypolimnetic inventory appears to be rapidly removed from the water column and returned to the sediments, presumably by precipitation and deposition of suspended matter to the lake bottom. After the fall turnover in 1999, however, there was a significant mercury release event whose source was not documented. The sediments are the likely candidate, given the magnitude of the release to the lake, but the mechanism for release was not documented. This event resulted in a doubling of the lake's output of mercury to the Seneca River for about a month's time. This release, unlike the fall turnover, may represent a means of escape for mercury in the lake's sediments. The scale of the release was relatively small, however, and most likely represents only a minor adjustment to the net amount of mercury captured by the lake on an annual basis.

Methylmercury

Methylmercury produced within the hypolimnion during stratification is released to the oxic waters of the lake as a result of fall turnover, unlike total mercury from the hypolimnion. The turnover process raises epilimnetic concentrations substantially, especially in the top 6 m of the lake. The increased methylmercury concentrations require weeks to dissipate and in fact remained elevated in the upper 6 m of the lake at the end of the study period, almost six weeks after fall turnover was complete. Based on the change in methylmercury concentrations in the water column during the fall of 1999, the lake inventory decreased by 400 g. During this period, 30 g were lost through the outlet, and based on 1992 sediment trap data, about 510 g were lost to the sediment. A mass balance estimate on the region above 9 m suggests that demethylation is a comparable loss mechanism to deposition (260 g). However, the mass balance estimate shows the estimated inputs and losses of methylmercury to be out of balance and that a significant source term is missing. Resuspension of lake sediments or in-lake waste deposit materials is a likely candidate for this source, representing an input load of 0.8 to 1.7 g/day.

6.1.3 Releases from the In-Lake Waste Deposit

As established in Chapter 4, Section 4.5 of this RI, Honeywell discharged large quantities of combined waste to Onondaga Lake (e.g., via the East Flume), including Solvay, sanitary, mercury, and organic wastes. These wastes resulted in deposits in Wastebed B and in Onondaga Lake. Over time, the deposition of the Honeywell wastes formed a large, shallow delta (which also extended the shoreline from Wastebed B into the lake; Chapter 3, Figure 3-9) that is exposed to surface water, as can be seen in the historic aerial photographs of the lake (Chapter 4, Figures 4-6 through 4-12).

As has been demonstrated in studies of other similar bodies of water, it is likely that this delta is being eroded by wind-driven waves (Aalderlink et al., 1984, Luettich et al., 1990, Hawley and Lesht, 1992; Latimer et al., 1999; Hawley, 2000; Lou et al., 2000). This is a possible reason for the changes seen between the 1951 to 1966 aerial photographs. Although horizontal currents are generally too small to influence suspended solids concentrations (Luettich et al., 1990), it has been suggested that in shallow lakes horizontal circulation currents can have an important effect on the redistribution of particulates resuspended by wind-induced wave action (Bailey and Hamilton, 1997). In Onondaga Lake, Owens and Effler (1996) have suggested that transport is dominated by wind-induced motion, except under calm conditions.

The contaminant distribution maps presented in Chapter 5, Section 5.2 illustrate that the waste deposit contains some of the highest concentrations of CPOIs in the lake. Because of these high concentrations, the waste deposit is a potential source of CPOIs to the lake system. There are many natural processes that could transport the CPOIs from the waste into the overlying water, including diffusion, groundwater advection, bioturbation, and wind-driven resuspension.

If the deposit is a source of CPOIs to the rest of the lake, then the surface water above the deposit should contain CPOIs at concentrations higher than the rest of the lake. If these CPOIs are transported due to diffusion or groundwater advection, then the concentrations in the overlying water should be consistently

greater than those of the deep basins of the lake and also be measurable during calm weather. If winddriven resuspension is also a release mechanism, then there should be increased concentrations of CPOIs and increased turbidity resulting from wind events.

6.1.3.1 Evidence of Mercury Releases from the In-Lake Waste Deposit

Resuspension of sediments in Onondaga Lake is a natural process, typically occurring in response to wind events and substantive tributary discharge events. However, the resuspension of contaminated sediments represents a pathway for the release of potentially sequestered contaminants from the sediments. For mercury, this pathway represents an important release mechanism. Similar concerns have been noted in other lakes. For instance, sediment resuspension in the Great Lakes has been reported to result in much greater fluxes than external inputs for many constituents (Eadie et al., 1984; Eadie and Robbins, 1987; Robbins and Eadie, 1991; Brooks and Edington, 1994). As a part of the RI data collection efforts, several different lines of evidence were obtained that suggest the occurrence of mercury sources in the nearshore areas. As will be discussed below, several results indicate a significant mercury source in the vicinity of the in-lake waste deposit. In the discussions that follow, evidence is presented suggesting resuspension of inlake waste deposit materials. Based on this evidence, a rough calculation is provided to estimate the magnitude of this flux, thereby allowing a comparison between this source and the other sources discussed previously in this section.

1992 Suspended Sediment Trap Investigation

Honeywell's 1992 RI included a series of suspended sediment trap deployments in the water column in the deep basins and shallower areas of the lake. Four stations were sampled in all, one from the center of each major lake basin (Stations W1 and W2), one off shore of the Honeywell lakeshore area (Station W15), and one off the Ninemile Creek delta (Station W16) (see Figure 6-12). As discussed in Section 6.1.2, each of the deep basin locations had two traps deployed, one at the bottom of the epilimnion and one at the bottom of the hypolimnion. The two stations closer to shore (Stations W15 and W16) had only one trap each, deployed at the bottom of the epilimnion (although the exact deployment depth was not reported). The following discussion is focused on these two traps and the deep basin epilimnetic traps.

The results from the southern basin for June to October 1992 indicate that the trap near the Honeywell shoreline (Station W15) had an average sediment flux that was five times greater and an average mercury flux that was 12 times greater than for the southern deep basin epilimnion trap (Station W1) (see Table 6-19). These data indicate that the littoral zone in the southern part of the lake is a source of both suspended solids and mercury to the entire lake, even though there is not a major tributary source in the area.

A similar comparison between the trap near the Ninemile Creek delta (Station W16) and the northern deep basin station (Station W2) for July to October (the traps were not deployed in the northern deep basin in June) indicated that the littoral zone trap had an average sediment flux that was four times greater and collected an average of about seven times more total mercury than the trap at the northern deep basin.

However, the size of the source appears to be about 35 percent smaller than the one in the southern deep basin, and the source could be either Ninemile Creek itself or the contaminated sediments in the delta.

Fall 1999 Lake Water Sampling Results

Although the fall 1999 mercury sampling program focused mainly on the deep basin stations, the September 28, 1999 sampling event included surface water samples from nine locations in the littoral zone and in the outlet in addition to the two deep basin stations (see Chapter 2, Figure 2-17). The results (Figure 5-146) for the September 28 event show that mercury concentrations at Station W53 (26.2 and 9.81 ng/L, field replicate pair, average of 18.2 ng/L) at the Ninemile Creek delta and Station W55 (103 ng/L) taken over the Honeywell in-lake waste deposit near Harbor Brook are higher than those in the rest of the lake (approximately 10 ng/L or less). The elevated concentrations relative to the rest of the lake suggest sources in these areas. The relatively higher concentration of mercury obtained at Station W55 suggests that the source in this area may be greater than that associated with Station W53, which is consistent with the differences noted in the suspended sediment trap data.

2000 Phase 2A Porewater Sampling Results

As part of the porewater investigation conducted in July 2000, lake water overlying each coring location was also obtained. Three coring sites (Stations S402, S405, and S344) were obtained from the area of the waste deposit, thus providing three lake water samples from this area as well. The total mercury concentrations obtained at these stations (19 ng/L, 264 ng/L, and 595 ng/L, respectively) were significantly higher than the lake water concentrations obtained at other core stations collected in the lake (average of 8.6 ng/L). These concentrations are also higher than surface water samples collected throughout the lake in the previous studies completed by Honeywell. These results again suggest that the waste deposit is a source of mercury to the rest of the lake.

2001 Phase 2B Surface Water Sampling Results

Based on the evidence obtained during the prior studies described above, surface water monitoring and sampling was conducted in the in-lake waste deposit area in November and December 2001 (see Chapter 2, Section 2.9). The sampling program was intended to investigate the possibility that the in-lake waste deposit acts as a source of mercury and other compounds to the lake. Because wind-driven resuspension was thought to be a major mechanism for this release of mercury from the waste deposit, the primary components of the monitoring program were wind (both velocity and direction) and turbidity (which would act as a surrogate for TSS/resuspension of sediment). Although there were no large wind events at speeds greater than 10 m/s during the monitoring period, the results from the mercury and TSS sampling on December 4 and 18, as well as the hourly turbidity values from UFI's Remote Underwater Sampling Station (RUSS) near the East Flume (see Chapter 2, Figure 2-20) from November 14 to December 26, support the following observations:

- A comparison of the hourly turbidity values at the East Flume RUSS station to wind direction (Figure 6-25) indicates that the turbidity levels are significantly higher (P-value <0.001) and more variable during west and north winds (between 270 and 50 degrees) as compared to levels for winds in other directions. Winds from between 270 and 50 degrees are hereinafter referred to as northwest (NW) winds.
- Under calm conditions on December 4, the total mercury concentration in water overlying the Honeywell in-lake waste deposit (10 ng/L) was approximately twice the concentrations observed in the surface water at the southern deep basin and the north shore (Chapter 5, Figure 5-152). This suggests that the Honeywell inlake waste deposit is a potential source, even under calm conditions.
- During a marginal NW wind event on December 18, the mercury concentration in the southern deep basin station remained at about 5 ng/L. However, the concentrations in the water overlying the waste deposit doubled to an average of about 20 ng/L, with the highest concentration at 49 ng/L at Station W66 (Figure 5-152). In addition, the area of increased concentration expanded from the northeastern edge of the waste deposit (Station W63) to Station W62, which is in 15 m of water about 200 m farther offshore (Chapter 5, Figure 5-152) than Station W63, suggesting that advection of resuspended particles might be important in transporting mercury from the area of the wastebeds.
 - The two most-pronounced NW wind/turbidity events occurred on December 15 and 21, 2001 (Figure 6-26). Data from those events indicated a delay of about eight hours between the onset of the wind event and the turbidity response. This delay might be related to the time needed to build up waves of sufficient energy to erode the sediment. Alternatively, it may be a delay related to the advective transport of the resuspended particles from the in-lake waste deposit to the RUSS location.
- There were two marginal wind events (December 7 and 18, 2001) (Figure 6-26) with moderate-to-strong NW winds (4 to 7 m/s), which did not exhibit the response described above. On both of these days, the wind was not sustained for more than eight hours and did not produce a turbidity response at the RUSS location. However, due to equipment malfunction, several hours of the turbidity data were missing for the December 18 event. These results, combined with the result of the strong wind events discussed above, suggest that measurable resuspension events require a sustained wind.
- There was a strong turbidity peak around December 1, 2001 (Figure 6-25) that did not have a correspondingly strong wind event. This elevated turbidity may be

due to a moderate flow event (about 350 cfs) in Onondaga Creek at that time. Onondaga Creek is the largest external source of TSS to Onondaga Lake. However, its discharge and associated turbidity plume typically flow to the northeast, away from the RUSS monitoring location used during this investigation. In the absence of strong winds, it is possible that the plume did not follow its normal path but instead traveled toward the study area. In the absence of direct observation or other explanatory data, such an event seems the likely cause of the observed turbidity peaks.

These observations are consistent with wind-driven resuspension of sediments from the in-lake waste deposit. Resuspension of littoral zone sediments are commonplace in most lakes, but the importance here lies in the highly contaminated nature of the sediments being resuspended.

6.1.3.2 Baseline Conditions for Northwest Winds

In order to estimate the magnitude of the mercury release attributable to wind-driven resuspension of the in-lake waste deposit, it is necessary to first summarize the wind conditions of the lake. Specifically, the critical NW wind speed and the background lake water turbidity should be established. The critical NW wind speed necessary for sediment resuspension was estimated from the RUSS data, but excluded the following:

- Turbidity response potentially associated with the December 2 flow event from Onondaga Creek.
- Turbidity and wind data representing the lag period between the onset of the wind event and the turbidity increase and the lag period between the end of the wind event and the turbidity decrease.
- Data from wind outside the 270 to 50 degree range; i.e., non-NW wind.

Based on this analysis, the minimum wind speed required for a sustained wind event to induce resuspension was established as 2.2 m/s (Figure 6-27). The average turbidity value for NW winds at or below this critical wind speed was estimated as 2.1 NTUs (nephelometric turbidity units). These values are derived from the observed change in the relationship between turbidity and wind speed as shown in Figure 6-27. The derivation of the turbidity values above 2.2 m/s is described below. It is important to note that while the calculations focus on winds that are sustained for a long period, it is possible to have high wind speeds that will resuspend particles in a very short period of time. Also, winds with speeds lower than this critical value sustained over long periods are not considered to contribute to resuspension since these winds are unlikely to provide sufficient energy to resuspend sediments.

6.1.3.3 Relationship Between Northwest Winds and Sediment Resuspension

A simple linear regression was used to establish a relationship between NW wind speed and resuspension (expressed as turbidity). In this analysis, only NW winds that were sustained for more than eight hours were used and the values used were averaged over the period of the event. In addition to the baseline estimate established above, the following four NW wind events were used for the regression analysis.

- November 16, 2001 Southwest winds blow at 5 m/s, swinging into the NW at 07:00 hours and increasing to about 6 to 7 m/s until 16:00 hours, and gradually dropping into calm conditions at 23:00 hours. The average wind speed (from 07:00 to 22:00 hours) was 5.0 m/s, and the turbidity increased to an average of 2.76 NTUs from 15:00 to 22:00 hours.
- November 28, 2001 Moderate (2 to 4.7 m/s) NW winds with some increase in turbidity (up to 4 NTUs). Average wind speed (from 02:00 to 17:00 hours) was 3.07 m/s, and average turbidity (10:00 to 17:00 hours) was 2.58 NTUs.
- December 15, 2001 Moderate to strong (3.2 to 8.3 m/s) NW winds until 16:00 hours. Average wind speed (00:20 to 16:00 hours) was 5.65 m/s, and average turbidity (07:00 to 16:00 hours) was 5.23 NTUs.
- December 21 into December 22, 2001 Strong (3 to 8.4 m/s) NW winds all day and continuing into December 22. Average wind speed (00:20 hours December 21 to 3:00 December 22) was 5.4 m/s, and the average turbidity during the stable period (11:00 December 21 to 3:00 December 22) was 5.22 NTUs.

Using the average results for each of the four NW wind events, along with the baseline conditions, the regression relationship between turbidity and wind speed for sustained NW winds with speeds above the baseline value of 2.2 m/s (Figure 6-27) is:

Turbidity [NTU] = $0.80 \times$ wind speed + 0.33, R² = 0.70

Effler and Perkins (1996) established a relationship between turbidity and TSS as follows:

Turbidity [NTU] =
$$0.63 \times TSS [mg/L] - 0.02$$

Combining the above equations, the suspended sediments concentration during sustained NW winds greater than 2.2 m/s can be estimated from the wind speed as:

TSS
$$[mg/L] = 1.27 \times \text{wind speed } [m/s] + 0.55$$

The TSS resuspended by the wind event can be obtained by subtracting the TSS value from its relationship with wind speed from the baseline TSS. This baseline TSS, which corresponds to the baseline turbidity of 2.1 NTUs, is 3.33 mg/L. This value is comparable to TSS values observed by Honeywell during the 1992 RI.

6.1.3.4 Estimation of Potential Advective Flux from Sediment Resuspension

Understanding and predicting the fate and transport of sediment resuspension during wind-wave events require numerical models that couple hydrodynamic and suspended solids mass conservation equations. Previous studies in sediment resuspension in shallow waters have used two-dimensional models (Ziegler and Lick, 1988; Gailani et al., 1991) and three-dimensional or quasi-three dimensional models (Galappatti and Vreugdenhil, 1985; Brun-Cottan et al., 2000; Lou et al., 1999, 2000) to predict suspended sediment dynamics. These models can be complicated and require data on several parameters. Hawley and Lesht (1992) reported that simple mass flux models can be used to explain local sediment resuspension events with reasonable accuracy. Recently, Lesht and Hawley (2000) successfully used empirical analysis as the basis of predicting observed sediment resuspension from relatively simple measures of hydrodynamic forcing. This observation by Lesht and Hawley (2000) was the basis for relating suspended material expressed as turbidity and wind speed, as described above.

The objective of this analysis is to estimate the potential advective flux of mercury resulting from the suspension of material from the Honeywell in-lake waste deposit during sustained wind events. The 2001 sampling results indicate that the region of high mercury water column concentrations expands beyond the in-lake waste deposit area during a marginal wind event, suggesting that advection from this area may be important. As noted in Chapter 3, the Honeywell in-lake waste deposit covers an area of about 65 acres, or 263,000 m² (Chapter 3, Figure 3-9). The waste deposit extends from the shoreline to about 300 m out into the lake, where the water depth is about 3.5 m.

Estimation of the advection of resuspended material requires information regarding both the wind-induced current moving the material from the waste area and the concentration of the material in the water column. Estimates of wind-induced currents have been reported for Onondaga Lake during drogue experiments done in 1987 (Owens and Effler, 1996). The results of these experiments indicate the following:

- Surface currents are about 2.5 percent of the wind speed (Table 6-28) and these currents are generally in the direction of the wind, with some offset in the nearshore areas.
- As the current approaches the shore, the current turns parallel to the shore so that no flow passes through the shoreline, except at points of inflow or outflow.
- The currents move in the opposite direction of the wind at depth to compensate for the windward movement of water at the surface.

When the currents at the surface down to a depth of 6 m are averaged, the depthaveraged currents are in the direction of the flow in the shallower shoreline areas, and opposite to the wind direction in the middle of the lake.

The following assumptions were made in this analysis:

- Significant advective transport of suspended material from the in-lake waste deposit occurs under sustained NW winds only.
- The turbidity and the derived suspended solids concentrations measured at the RUSS location represent the equilibrium suspended material concentrations in the waste deposit area during resuspension events.
- The in-lake waste deposit covers an area of about 300 m by 800 m, and the average depth of water above this mass is 2 m. Because NW winds can cause currents along both the length and width of the waste mass, the average length of 550 m is used in estimating cross sectional areas.
- The suspended sediments above the baseline values have concentrations equivalent to the average mercury concentration of 18.1 mg/kg of the surface sediments (0 to 0.15 m) in the waste deposit area.
- The suspended particles are assumed to be very small so that their motions relative to the ambient water fall into the Stokes' range. Thus, the velocities of the particles are equivalent to the water flow velocity. Complications introduced by sediment cohesion are neglected.
- Because hydrodynamic model predictions of water circulation at Onondaga Lake (Owens and Effler, 1996) indicate that the surface current boundary layer along the shoreline extends to the bottom, it is assumed that the magnitude of the mean horizontal current will be approximately half the surface velocity. Therefore, for a surface current of about 2.5 percent of the wind speed, the mean horizontal current over the waste deposit area is assumed to be 1.25 percent of the wind speed.
 - The linear regression derived above between turbidity or TSS and wind speed can be extrapolated to wind speeds up to 17 m/s, which corresponds to an average current speed of about 0.22 m/s. Note that Lesht and Hawley (2000) obtained a linear regression fit between suspended material and average current speed for current speeds as high as 0.30 m/s in the Great Lakes.

The calculation of potential advective fluxes of suspended material is provided below for three different wind-speed categories (addressed below). For each category, the potential advective flux is estimated as:

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Advective Flux = C \times Q
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where :

- C = the average total mercury concentration in the water column above the waste deposit, which can be estimated as the product of the TSS concentration and the sediment concentration of 18.1 mg/kg.
- Q = the advective flux of water, which is $1.25\% \times \text{wind speed} \times \text{cross}$ sectional area of $1,100 \text{ m}^2$ (depth of 2 m by average length of 550 m).

Category 1: For wind speed between 0 and 2 m/s

Under this category, there is no resuspended material and any elevated mercury is due to groundwater advection or other non-wind-event mechanisms. In this case, the measured mercury concentration of the water column during baseline conditions can be used for the calculation of baseline load. The water column mercury concentrations in the waste mass area (10 ng/L) is about 5 ng/L greater than average concentrations in the deep basin. Using the net concentration difference of 5 ng/L (or 5×10^{-6} g/m³) and average wind speed of 1 m/s (or 86,400 m/day), the advective flux is:

Advective Flux = 5×10^{-6} g mercury/m³ × 1.25% × 86,400 m/day × 1,100 m² = 5.9 g mercury/day

Over the stratified period of 120 days, the total background flux is about 710 g of total mercury. This is of the same order-of-magnitude as the 310 g for the period calculated for the groundwater flux from the Wastebed B/Harbor Brook site, and compares even better with the 460 g calculated for groundwater advection of porewater through the waste deposit. This load does not represent a portion of the resuspension load. The similarity of the estimates of the background advective flux out of the in-lake waste deposit and the calculated flux out of the in-lake waste deposit, based on groundwater advection, suggests a possible link between the two fluxes and adds support to the estimated magnitude of the resuspension flux.

Category 2: For wind speeds between 3 and 5 m/s

An average wind speed of 4 m/s (345,600 m/day) is used in this estimate. The predicted TSS concentration using the TSS-wind speed relationship described above is 5.6 mg/L. The resuspended material, which is the mass of TSS above the baseline of 3.3 mg/L, is estimated as:

5.6 mg/L - 3.3 mg/L = 2.3 mg/L

This resuspended material has a mercury concentration of 18.1 mg mercury/kg TSS (or 18.1×10^{-6} g mercury/g TSS). The advective flux under this conditions is:

Advective Flux = $2.3 \text{ g TSS/m}^3 \times 18.1 \times 10^{-6} \text{ g mercury/g TSS} \times 1.25\% \times 345,600 \text{ m/day} \times 1,100 \text{ m}^2 = 198 \text{ g mercury/day}$

Based on the six-week monitoring program in 2001, sustained NW winds at speeds of 3 to 5 m/s occurred about 5 percent of the time. For the 120-day stratified period, the potential transport of mercury under this wind condition is:

198 g mercury/day \times 120 days \times 5% = 1,190 g, or about 1,200 g for the period.

Category 3: For wind speeds between 6 and 17 m/s

The average wind speed is assumed to be 11.5 m/s (993,600 m/day). The predicted TSS concentration using the TSS-wind speed relationship derived above is 15.2 mg/L. The resuspended material, which is the TSS value above the baseline (3.3 mg/L), is given as:

15.2 mg/L - 3.3 mg/L = 11.9 mg/L (or 11.9 g TSS/m^3).

The advective flux under this condition is:

Advective Flux = $11.9 \text{ g TSS/m}^3 \times 18.1 \times 10^{-6} \text{ g mercury/g TSS} \times 1.25\% \times .993,600 \text{ m/d} \times 1,100 \text{ m}^2 = 2,940 \text{ g mercury/day}$

Based on the six-week monitoring program in 2001, sustained NW winds at speeds of 6 to 17 m/s occurred about 5 percent of the time. For the 120-day stratified period, the potential transport of mercury under this wind condition is:

2,940 g mercury/day \times 120 days \times 5% = 17,655 g, or about 18,000 g for the period.

Summary

Combining the results from the second and third categories (3 to 17 m/s), the total potential advection flux of mercury from the Honeywell in-lake waste deposit is roughly 20,000 g. As indicated by the calculations given above, the vast majority of this flux is the result of the highest wind-speed events. Distributing this flux over the entire period of stratification yields a mean daily input via resuspension of about 170 g/day.

As stated at the beginning of Section 6.1.3, these estimates are meant to indicate the order-of-magnitude of the mercury loads caused by resuspension of the in-lake waste deposit, since data limitations prevent

further refining of this estimate. Among other issues, it is likely that the frequency of resuspending wind events during the period of stratification (summer) will be substantively lower than the observed frequency during the 2001 sampling event (late fall). There are other simplifications in this calculation that may also modify the flux estimate. Nonetheless, these estimates suggest that transport of resuspended mercury is of the same magnitude as the difference between the other quantified inputs and the quantified outputs of the epilimnion.

This analysis should not be construed as a definitive estimate of the monthly or annual resuspension flux resulting from the in-lake waste deposit. Rather, it is intended to indicate the scale of its role in the mercury budget for the lake. This analysis shows that this deposit of Honeywell wastes in the lake proper has not been permanently sequestered by natural processes, but rather is available and actively involved in sustaining the mercury inventory in the water column of the lake. This assertion is supported by both the direct measurements of water quality around these deposits as well as by the rough estimate of flux provided here. Even if the flux estimate developed here for the period of stratification is an order-of-magnitude too high, this flux (2,000 g as opposed to 20,000 g) would still be equivalent to the combined fluxes of Ninemile Creek, Onondaga Creek, and the Metro facility (2,200 g) for the same period and, thus, must be considered a significant source of mercury to the water column.

6.1.4 History of Mercury and Other Metals in the Sediments

Analysis of thinly sectioned ("high resolution") sediment cores can give temporal information regarding historical inputs of particle reactive contaminants to the sediment column. In highly depositional areas with continuous net sediment accumulation, it may be possible to assign a date of deposition to the individual intervals of the sediment core, thus allowing the determination of trends in contaminant inputs. This dating may be done with the analysis of particular radionuclides, as well as contaminants, if historical input is known. In the sediment cores discussed in this section, cesium-137 (¹³⁷Cs) will be used, in addition to mercury and lead, for dating purposes. ¹³⁷Cs is a particle reactive radionuclide that was introduced to water bodies in about 1954 through global fallout from the testing of nuclear weapons. In about 1963, just prior to the banning of this testing, there was a peak in ¹³⁷Cs fallout (Ritchie and McHenry, 1990).

In this section, data from high-resolution cores collected by Honeywell/Exponent and Rowell (1992) will be discussed. These cores were analyzed for ¹³⁷Cs and inorganics. ¹³⁷Cs data were reported in units of decays per minute per gram (dpm/g). General discussions of the fate of inorganics other than mercury are provided in Section 6.2. This discussion provides an overview of the history of toxic metal contamination in the lake. Thus, all of the metals are discussed together here. No organic contaminants were analyzed as part of the high-resolution coring investigations and thus are not discussed here.

Honeywell/PTI collected six high-resolution sediment cores: five in 1992 and one in 1996. Figure 6-28 shows the ¹³⁷Cs profiles from two of these 1992 cores, including S90, which was collected from the northern deep basin, and S51, which was collected from the southern deep basin. The first detection and the peak of ¹³⁷Cs are seen at the same depth intervals from both of these cores, at 35 to 37 and 25 to 27 cm, respectively. Unfortunately, ¹³⁷Cs was only analyzed in every other depth interval between 10 and 57

cm in S51 and 10 and 55 cm in S90. Because of this, the ¹³⁷Cs peak has not been well constrained, and it may actually be one interval higher or lower in the sediment cores. Because of the lack of ¹³⁷Cs data, a sediment accumulation rate has not been estimated for the length of these cores; however, it can be said that sediment from 1954 was deposited at an approximate average depth of 37 cm, and sediment from 1964 was deposited at an approximate average depth of 26 cm. Between these two intervals, there was an average sediment accumulation rate of approximately 1.1 cm/yr.

The data from the other high-resolution sediment cores collected by Exponent will not be discussed in this section because the ¹³⁷Cs profiles indicate a discontinuous net sedimentation rate. However, in order to show the variability in the sediment accumulation rate throughout the lake bottom, the ¹³⁷Cs data for these other cores are presented in Figure 6-29. These plots help illustrate the variability in deposition rates within the lake. This is important with respect to contaminant burial and resuspension. It is important to note that the analysis of a few sediment cores from the deep basins, typically in areas with high net sediment accumulation, and the estimation of an average sediment accumulation rate cannot be applied to the entire lake bottom. Contaminant burial may take place within the deep basins; however, in areas with little net sediment accumulation, this burial may not occur, or it may occur at a much slower rate. In some areas, resuspension will be a more significant issue, particularly for sediments in more shallow regions of the lake.

Rowell (1992) collected five cores from Onondaga Lake. The results from two gravity cores, S-1 (south deep) and N-1 (north deep), will be discussed here. With the use of diatom analysis, isotopic dating, and pollen analysis, Rowell estimated the average sediment accumulation rates in the northern basin to be 0.21 cm/yr from 1822 to 1884, 0.35 cm/yr from 1884 to 1964, and 0.83 cm/yr from 1964 to 1988. The apparent increase in sedimentation rate for 1964 to 1988 is likely due to under-compaction of the shallower sediments. By adding one more constraint to the dating, the first detection of ¹³⁷Cs, an estimate of the average sediment accumulation rates against mercury and lead analyzed in the same core supports these average rates (Figure 6-31). In the lead profile, the sharp decline in concentration is observed at about 1970, the year in which the phasing out of leaded gasoline began. However, the decline may also be correlated with the cessation of some unknown discharge to the lake.

In the mercury profile, there are two time horizon markers, 1947 and 1970. At approximately 1947, the levels of mercury increase to well above background levels. There are small fluctuations between 1947 and 1970, where there is a sharp decline that coincides with a 95 percent reduction in mercury loading (Rowell, 1992). The gravity core collected by Rowell from the southern basin was not presented this way because fewer depth intervals were analyzed for metals. The contaminant time markers could not be well constrained. Samples were analyzed about every 1.3 cm in the northern basin core and about 5.1 cm in the southern basin core.

Figures 6-32 through 6-35 show nickel, cadmium, mercury, chromium, lead, copper, and zinc concentrations as a function of depth in the four deep basin cores that showed a continuous net sedimentation rate (Rowell's 1988 southern and northern basin cores and Honeywell/PTI's 1992 southern and northern basin cores). There are similar trends in the inputs of these metals into Onondaga Lake.

Additionally, as seen in Figures 6-32 and 6-33, there is an increase in metals concentrations near the surface of Rowell's cores from both the northern and southern basins. This increase is not seen in Honeywell's cores.

However, there does seem to be a correlation between this increase in mercury in sediments and mercury in fish tissue (Rowell, 1992). Figure 6-36 shows the trend in mercury per length of smallmouth bass (*Micropterus dolomieui*) between 1970 and 1990. The significant decline after 1970, the year in which there was a 95 percent reduction in mercury loading to the lake (Rowell, 1992), is reflected in the fish data as well as in the sediment cores. Between 1986 and 1987, mercury per length of fish increased from 0.003 to 0.005 mg/kg-mm. Between the average sediment depths of about 4 and 3 cm (dated at approximately 1983 and 1985, respectively) in Rowell's core from the northern deep basin, mercury increased from 1.5 to 8.4 mg/kg. This increase was also seen in the core collected from the southern basin, which exhibited a mercury concentration of 1.7 mg/kg at an average depth of 10.8 cm. This increased to 9.9 mg/kg at an average depth of 5.7 cm. The increase observed in the metals analyzed in Rowell's cores was also observed in the ¹³⁷Cs data. It is possible that this increase in concentration was caused by a decrease in sediment deposition in the lake. The fact that the ¹³⁷Cs concentrations also rise near the surface suggests that a change in deposition rate was likely resulting from a decreased rate of calcite precipitation as a result of the closure of the Honeywell facilities and the cessation of ionic waste discharges to the lake.

It is likely that sediment loads to the lake were reduced after the closure of the Honeywell production facilities in 1986. Hairston et al. (1999) collected three high-resolution sediment cores at 17 m from the saddle region in Onondaga Lake in 1995, 1996, and 1997. These cores were dated using ²¹⁰Pb. From the most recent core collected in 1997, the average net sediment accumulation rate from 1967 to 1986 was about 0.97 cm/yr. This decreased to 0.77 cm/yr between 1986 and 1997, assuming the top of the core represented the year of collection. This decrease in average net sediment accumulation rate may reflect the closure of the Honeywell facilities. However, it should again be noted that an accumulation rate estimated from one core should not be applied to the entire lake bottom. Dateable sediment profiles collected in areas with a high net sedimentation rate are not indicative of sediment accumulation rates in all areas.

Although sediment deposition rates are not constant across all cores, the profiles document some important trends in metal chemistry in the lake. In all instances, metal contamination in the lake has declined substantially since the 1970s and early 1980s. Thus, it would appear that most of the major external sources of metal contamination to the lake have been greatly reduced. Nonetheless, recently deposited concentrations of all the metals examined, including mercury, still greatly exceed background concentrations, indicating that either residual in-lake contamination or ongoing external loads are preventing a more rapid recovery of the lake. The recent rise in metals concentration in the surficial sediments in the Rowell cores suggests that significant changes have occurred in the lake's chemistry, almost certainly as a result of the cessation of ionic waste discharges. The fact that this effect is not observed in the Honeywell/PTI cores suggests that these cores represent slower deposition environments, such that the cores are unable to provide sufficient temporal resolution.

6.2 Transport and Fate of Non-Mercury Chemical Parameters of Interest in Onondaga Lake

This section discusses the general characteristics of environmental transport and fate of non-mercury CPOIs and presents estimates of loadings of these CPOIs to Onondaga Lake. Where possible, available data were used to calculate estimates of the input and output fluxes to and from the lake for metals other than mercury, BTEX, chlorinated benzenes, PAHs, PCBs, and PCDD/PCDFs. It should be clarified that the calculated values presented in this section are estimates intended to provide an order-of-magnitude characterization of the potential source or sink. For each class of CPOIs, annual fluxes were estimated for tributaries, groundwater advection, porewater advection, porewater diffusion, precipitation, volatilization, and outflow, while fluxes for the release of resuspended materials from the Honeywell in-lake waste deposit, and particle settling were estimated for the stratified period only.

6.2.1 Methods Used in Non-Mercury Chemical Parameters of Interest Loading Calculations

Where possible, consistent methods and data sets were used to estimate the loadings to Onondaga Lake for each of the compound groups discussed. There were instances where the availability of data limited the use of a particular method. In these cases, an alternative method was used and will be discussed where appropriate. Below is a discussion of the methods used in the calculations.

6.2.1.1 Tributary Loads

The loads from tributaries were estimated using the surface water concentrations and the average annual flow for each tributary. The equation used is:

$$F_{T=}C_w \times q_T$$

where:

 $F_T =$ tributary flux $C_w =$ average water concentration $q_T =$ average annual flow of the tributary.

There are some cases when there were no detections or no analyses of the contaminants in the surface water, but there were detections in the sediment. In this instance, an equilibrium partitioning model was used to estimate the water concentration from the sediment concentration. Assuming that the water column and the sediments are in equilibrium, the concentration in the water column was estimated using:

$$C_{W} = \frac{C_{sed}}{Koc \times foc} + C_{sed} \times TSS$$

where:

C_w	=	total water column concentration (mg/L)
C_{sed}	=	sediment concentration (mg/kg)
K _{oc}	=	partition coefficient (L/kg)
f_{oc}	=	fraction organic carbon
TSS	=	total suspended solids (mg/L).

The first part of this equation, which contains the terms K_{oc} and f_{oc} , provides the dissolved concentration of the contaminant. The second term, which contains the TSS, estimates the particulate-phase concentration. The total water concentration of the CPOI from this model was compared to the reported detection limit of the CPOI in surface water. When the model-estimated concentration was consistent with the detection limit (i.e., estimated concentration was equal to or lower than the detection limit), the modelestimated value was used in the load calculations. When the model-estimated concentration was higher than the detection limit, the concentration value was set to half of the reported detection limit. In the latter instance, the presence of the contaminant in the sediments of the tributary is still considered proof that the contaminant is present in the water column. When a CPOI was not detected in both the water column and the sediment, no loadings were estimated for the CPOI.

6.2.1.2 Groundwater Advection

The CPOI loadings via groundwater were calculated by multiplying the groundwater discharge with the average concentrations from the selected wells. Groundwater loads were only estimated for the area between Tributary 5A and Harbor Brook. Details on the groundwater discharge along this area and the methods of discharge calculations are given in Section 6.1.1.3.

6.2.1.3 Flux from Sediment Porewater

Two sediment porewater fluxes, including porewater diffusion and porewater advection, were estimated for non-mercury CPOIs. Porewater diffusion was estimated on a whole-lake basis, while porewater advection was estimated only for the area between Tributary 5A and Harbor Brook in the littoral zone.

The concentration gradient between the sediment porewater and the overlying water may cause a fraction of the contaminants to be released to the water column by diffusion. Methods on estimating diffusion coefficients and the diffusive flux, were discussed in Section 6.1.1.4. Surface sediment (0 to 0.02 m) concentrations were used to estimate the porewater concentration based on partition coefficients, as follows:

 $C_{porewater} = \frac{C_{sed}}{Koc \times foc}$

In order to estimate the porewater diffusion flux, the littoral and profundal zones of the lake were divided into various segments (see Figure 6-6), as follows:

$$C_{AP} = \frac{C_{air}}{K_{H'}}$$

The littoral zone segments were Onondaga Creek to the East Flume, the East Flume to Tributary 5A, Tributary 5A to Ninemile Creek, and Ninemile Creek to Onondaga Creek.

The profundal zone segments were the northern and southern deep basins, based on the water classification boundary.

The average sediment concentrations for each segment were used to estimate the corresponding porewater concentrations from which the diffusive fluxes were calculated. The total diffusive flux is the sum of individual diffusive fluxes from the sub-zones.

A porewater advection flux was estimated for the shoreline between Tributary 5A and the East Flume as well as for the shoreline between Harbor Brook and the East Flume. In this case, the groundwater discharge along this area estimated in Section 6.1.1.3 was multiplied by the estimated sediment porewater concentration for each CPOI, and the results were compared with the estimates from groundwater advection from the upland sites.

6.2.1.4 Precipitation

The input of CPOIs to Onondaga Lake via precipitation to the lake surface was estimated using the rainfall rates for the Syracuse area (44 inches in 1992 [NOAA, 1992]), surface area of the lake $(1.2 \times 10^7 \text{ m}^2)$, and the concentrations of the CPOIs in the precipitation, where available. For the CPOIs without precipitation concentrations, the aqueous phase of the CPOI was estimated from the air concentration using the following air-water equilibrium equation:

where:

C_{AP}	=	concentration in the aqueous phase
C_{air}	=	concentration in air (gas phase)
$K_{H'}$	=	dimensionless Henry's Law constant.

6.2.1.5 In-Lake Resuspension

Details of the estimation of advective flux of resuspended sediments was described in Section 6.1.3. Areaweighted average concentrations of non-mercury CPOIs in the surface sediments in the in-lake waste deposit were calculated using a Thiessen polygon declustering technique. These concentrations were used to estimate the potential advective flux under the two wind categories: 3 to 5 m/s and 6 to 17 m/s, which were combined to give the total flux due to resuspension during the stratification period. As noted in Section 6.1.3, the estimate of resuspension and release to the lake from this area illustrates the potential importance of this pathway for the CPOIs involved.

6.2.1.6 Volatilization

Volatilization was calculated using the two-phase resistance model described in Section 6.1.2.1. Average concentrations of CPOIs in the surface water of the lake were used, along with literature values of CPOI concentrations in ambient air. Ambient air concentrations for most CPOIs were obtained from the Agency for Toxic Substances and Disease Registry (ATSDR) toxicological profiles. The estimates were adjusted for the assumption that there are three months of ice cover to the lake, and the temperature for the littoral zone was assumed to be 20°C during the non-winter period. In some cases where there were no surface water data available (hexachlorobenzene, PAHs, PCBs, and PCDD/PCDFs), the littoral zone surface sediment concentrations were used to estimate the dissolved-phase surface water concentration using the partitioning model described above under tributary load estimates.

6.2.1.7 Outflow

The amount of CPOIs exiting Onondaga Lake through the outlet was calculated by summing the volume of water entering the lake each day during the study period and multiplying by the average northern deep basin surface water concentration of the CPOIs (0 to 3 m). When there were no available surface water data, the northern basin profundal zone surface sediment concentrations were used to estimate surface water concentrations for the outlet. As discussed in Section 6.1.2.1, the backflow rate was assumed to be 7 percent of the lake discharge.

6.2.1.8 Particle Settling Flux

The loss of CPOIs from the water column via settling of particles was calculated based on the measurements from the sediment traps during the stratification period. Details of sediment trap results can be found in Section 6.1.2.1. The particle settling flux was estimated by multiplying the TSS flux for the lake with the average concentrations of surface sediment (0 to 0.02 m) in the littoral zone. The surface sediment concentration for the littoral zone was estimated using the area-weighted average of the surface sediment concentrations for the various littoral sub-zones.

6.2.2 Metals Other than Mercury

This section discusses the inorganic CPOIs other than mercury, including cadmium, chromium, copper, lead, nickel, and zinc. A correlation analysis and principal components analysis were performed on the concentrations of these metals detected in Onondaga Lake sediment samples collected in 1992 and 2000 (see Appendix I). The results of these analyses showed that the metals can be divided in two groups based on their distributions. In the first group, lead, cadmium, zinc, and copper have similar distributions, and in

the second group, chromium and nickel have similar distributions. The similar distributions of the metals in each group can also be seen in Chapter 5, Figures 5-4 through 5-9.

The correlations and similar spatial distributions suggest that these metal groups represent classes of contaminant discharges with similar point sources and similar geochemistries within the lake. Thus, only one member of the group needs to be examined closely in order to characterize the sources, fate, and transport of the entire group. For the first metals group, lead was selected for analysis, and chromium was selected for the second group.

There are numerous industrial uses for these metals and their alloys, as follows:

- Cadmium is corrosion-resistant and is used as a protective coating for metals (e.g., galvanization). Its most common use is in nickel-cadmium (Ni-Cd) batteries, but it is also used as a stabilizer in PVC; electronics; and in aircraft and automobile manufacturing. Cadmium compounds are also used as fungicides, insecticides, and nematocides (Sittig, 1991; ATSDR, 1999b).
- Chromium is often used in the manufacture of dyes and pigments, as a wood preservative, in the production of stainless steels, chrome plating, and as lining for high-temperature industrial furnaces (ATSDR, 2000a).
- Copper is used to make metal (e.g., pipes, pennies, wire); in water treatment; to treat some plant diseases; and to preserve wood, leather, and fabrics (ATSDR, 1999d).
- Lead has many different uses, such as in the production of batteries, ammunition, metal products (solder and pipes), and devices to shield X-rays. Because of health concerns, the use of lead in gasoline, paints and ceramic products, caulking, and pipe solder has been dramatically reduced in recent years (ATSDR, 1999a).
- Nickel is often used in alloys (copper, iron, and chromium) as a heat exchanger, electrodes for welding, protection against corrosion and oxidation from acids and salts, and for strength and corrosion resistance over large temperature ranges (ATSDR, 1997a).
- Zinc has many commercial uses as coating to prevent rust, in dry cell batteries, and mixed with other metals to make alloys such as brass and bronze. Zinc compounds are widely used in industry to make paint, rubber, dye, wood preservatives, and ointments (ATSDR, 1994).

The presence of these metals in Onondaga Lake and its tributaries is the result of discharges from the various industrial operations in the lake's watershed.

6.2.2.1 Environmental Persistence and Fate

In aqueous systems, most metals speciate and form complexes that govern their solubility, mobility, and fate. In most aquatic systems, the behavior of metals is most dependent on the pH, the redox state, and the presence of other chemicals. Lead, copper, zinc, and cadmium behave similarly and would be expected to be relatively immobile in the sediment of Onondaga Lake. These four metals exist dominantly as divalent cations in solution that are soluble under oxidizing, low-pH conditions; however, in higher-pH environments, their solubilities depend on the presence of carbonates or oxide/hydroxides.

Under lake conditions with a relatively high pH (7 to 8) and high concentrations of dissolved carbonate species, relatively insoluble complexes will typically be formed. Under reducing conditions in the presence of sulfur, these metals will produce relatively insoluble sulfides. If no sulfur is present, they will behave as they do under oxidizing conditions (Drever, 1997). Chromium and nickel will also likely be immobile in the sediment of Onondaga Lake. Within neutral and alkaline pH ranges, chromium will exist as Cr^{3+} , which strongly adsorbs to particles.

6.2.2.2 Inputs to Onondaga Lake

Tributary Loads

Average annual loadings of lead and chromium were calculated for the major tributaries of Onondaga Lake using the average US Geological Survey (USGS) annual flows and average surface water concentrations collected during all flows by Honeywell/PTI in 1992, as discussed in Sections 6.1.1.1 and 6.2.1. Half the detection limits were used to estimate concentrations in the calculations when samples contained non-detect results. Lead loadings were estimated to be on the order of 3,000 kg/yr, with 70 percent from Ninemile Creek, Bloody Brook, and Onondaga Creek (Table 6-29). It should be noted that the estimate for Bloody Brook was based on only two samples, with only one being a detection (44 μ g/L). Tributary loadings of chromium were estimated to be on the order of 1,800 kg/yr, with approximately 65 percent from Ninemile Creek, Tributary 5A, and Onondaga Creek.

Groundwater Advection

Groundwater data, as reported in the Semet Residue Ponds RI (O'Brien & Gere, 1991), Willis Avenue RI (O'Brien & Gere, 2002e, under review), and the recent pumping tests report (O'Brien & Gere, 2002f), from wells along the lakeshore were used to estimate the annual chromium and lead groundwater advection loading to Onondaga Lake. Details of the model used to calculate groundwater flux to the lake are discussed in Section 6.1.1.3. With the use of this model, it was estimated that groundwater from the shoreline between Tributary 5A and Harbor Brook contributes both chromium and lead on the order of 46 kg/yr (Table 6-30).

Groundwater flowing through the Willis Avenue lakeshore area transports approximately 50 percent of the lead and chromium input to the lake along the Honeywell lakeshore area. The groundwater from the

Wastebed B/Harbor Brook lakeshore area contributes approximately 8 and 18 percent annually of the total chromium and lead, respectively. Contribution from the I-690 drainage pipes was estimated to be on the order of 0.2 and 0.08 kg/yr of chromium and lead, respectively (Table 6-31).

Flux from Sediment Porewater

The diffusive flux of metals from porewater was not estimated due to the lack of sufficient data to constrain the calculation. The behavior of metals is highly dependent on number of geochemical factors, including the presence of other compounds, redox potential, and pH. Thus, a porewater flux estimate was considered too uncertain to be useful for the discussion. However, it is likely that under typical geochemical conditions in Onondaga Lake, these metals would have a low solubility and would be relatively immobile within the porewater. Due to the historical inputs to Onondaga Lake of calcium carbonate-contaminated Solvay waste from the Honeywell facilities, the lake has a high carbonate content. In sediment samples collected in 1992, the average carbonate content was 55 percent (dry weight). In samples collected in 2000, this average was 62 percent (dry weight). This would be expected to have a strong suppressive effect on the mobility of the metals within lake porewater, as well as in the water column.

Precipitation

No data were found for concentrations of lead and chromium in rainfall for the Syracuse area. In order to get an order-of-magnitude estimate of the annual loading due to rainfall, concentrations reported in a study performed in New Castle, New Hampshire were used (Pike and Moran, 2001). Concentrations of 0.135 and 1.31 μ g/L were used for chromium and lead, respectively. Using rainfall data from 1992 (NOAA, 1992), as discussed in Section 6.2.1, a rainfall estimate of 1.33×10^7 m³ was used in this calculation. The annual loading of lead and chromium to Onondaga Lake was estimated to be on the order of 17 and 2 kg/yr, respectively (Table 6-31).

In-Lake Resuspension

Resuspension of contaminated sediments can contribute to contamination within the water column. A model was developed for mercury to estimate the loadings due to resuspension over the stratified period. This model is addressed in detail in Section 6.1.3. For the metals discussion, this model was applied to area-weighted average surface sediment concentrations from the 0 to 2 cm interval to estimate the average chromium and lead loadings to Onondaga Lake over the stratified period via resuspension. It was estimated that resuspension contributes approximately 67 kg of chromium and 121 kg of lead over the stratification period (Table 6-31).

6.2.2.3 Losses from Onondaga Lake

Outflow

Both lead and chromium were detected in surface water samples collected in 1992 and 1999 from 0 to 3 m in the northern basin of the lake at average concentrations of 1.2 and 1.8 μ g/L, respectively. Half detection limits were used to represent non-detect results. Estimating the annual discharge of lead from the lake, as discussed in Section 6.2.1, resulted in a discharge rate on the order of 600 kg/yr. Approximately 900 kg of chromium is discharged per year (Table 6-32).

Particle Settling

In order to estimate chromium and lead loadings to the lake water column via particle rain, the average concentrations from the surface sediment in the littoral zone were used, as discussed in Section 6.2.1. These values were used in the calculations rather than the surface water concentrations because the high number of non-detects in the surface water samples indicated that the sediment data would be more reliable than the surface water data. This particle deposition is a function of sediment loadings from tributaries and resuspended particles.

A particle rain rate of 9.7×10^6 kg of suspended sediment was estimated for the stratification period, as presented in Section 6.1.2. The estimated loading of chromium to the lake bottom via particle rain was on the order of 3,400 kg for the stratified period (Table 6-32). This estimate is on the same order as that for the tributaries (3,000 kg/yr); however, it should be noted that the particle settling rate was estimated over the stratified period, and the tributary loadings were estimated annually. The loading of lead over the stratified period was estimated to be on the order of 1,000 kg (Table 6-32). These flux estimates are limited to the stratified period, due to the lack of appropriate data during other times of the year.

6.2.2.4 In-Lake Processes

In aqueous systems, these metals speciate and form complexes that govern their solubility, mobility, and fate. In most aquatic systems, the behavior of metals is most dependent on pH, the system's redox state, and the presence of other chemicals. Based on the behavior of the metals discussed and the conditions in and around Onondaga Lake, a large fraction would most likely have a tendency to form low-solubility compounds and eventually settle with particles to the lake bottom. Consistent with this, and based on the loading estimates discussed above, the dominant means of transport of these metals into Onondaga Lake is through the tributaries. Groundwater loading is relatively insignificant when compared to tributary input (about 2 percent). The dominant means of removal from the lake is through particle settling.

6.2.2.5 In-Lake Distribution and Likely Sources

As discussed in Chapter 5 and depicted in Figures 5-5 and 5-8, chromium and nickel contamination in Onondaga Lake is widely distributed. Consistent with the contaminant distribution maps, potential sources

appear to be Tributary 5A, Ley Creek, Onondaga Creek, and Ninemile Creek, with the highest levels extending from Ninemile Creek, Tributary 5A, and Onondaga Creek. Historically, steel and other metal-related industries have existed near Tributary 5A and Ley Creek.

Also as discussed in Chapter 5 and depicted in Figures 5-4, 5-6, 5-7, and 5-9, the cadmium, copper, lead, and zinc contamination is widely distributed over the lake bottom. The loading estimates for lead (discussed above) determined that about 66 percent of the total tributary loadings originated from Ninemile Creek, Ley Creek, and Onondaga Creek. Bloody Brook also had a high estimate, at approximately 22 percent of the total tributary load of lead (664 kg/yr); however, this was based on only two samples, one in which no lead was detected.

6.2.3 Benzene, Toluene, Ethylbenzene, and Xylenes

This section discusses the fate and transport of BTEX in Onondaga Lake. Benzene, toluene, and xylenes compounds were produced at the benzol facility located on the Honeywell Main Plant and used at the Honeywell Willis Avenue plant in the production of chlorinated benzenes. They are also used in a number of industrial processes including the manufacture of other chemicals, some rubbers, paints, paint thinners, lubricants, pesticides, fuel oil, and as cleaning solvents. Typically, BTEX contamination occurs through atmospheric release from burning coal and oil, motor vehicle exhaust, or from direct release into water and soil via disposal of products containing BTEX (ATSDR, 1995a, 1997b, 1999c, and 2000b).

6.2.3.1 Environmental Persistence and Fate

Generally, the mechanisms governing the fate and transport of BTEX compounds will be the compounds' tendency to partition into the vapor phase. Microbial degradation and photooxidation may also contribute significantly to the loss of these compounds. Benzene, with the highest vapor pressure (95.2 mmHg, solubility (1,780 mg/L), and Henry's Law constant (1.75×10^3) , will tend to volatilize more readily than the others. Toluene, ethylbenzene, and xylenes would also be expected to volatilize; however, their affinity for the vapor phase (vapor pressures of 28.4, 9.53, and 6 to 16 mm Hg; solubilities of 535, 177, and 130 mg/L; and Henry's Law constants of 5.26×10^2 , 1.69×10^2 , and 1.7×10^2 for toluene, ethylbenzene, and xylenes, respectively) is not quite as strong as that of benzene.

6.2.3.2 Inputs to Onondaga Lake

Tributary Loads

Due to the vapor pressures of BTEX compounds and their preferential partitioning into the air from the water column, tributary loadings to Onondaga Lake are expected to be relatively insignificant since there is ample opportunity for volatilization to occur in these lotic environments. Average annual loadings of BTEX compounds were calculated for the major tributaries of Onondaga Lake using the average USGS annual flows and average surface water concentrations collected during all flows by PTI in 1992. In some of the tributaries, there were no detections of BTEX compounds in the surface water. As an alternative

method of estimating water concentrations, the surface water concentrations were estimated on the basis of the equilibrium partitioning model presented in Section 6.2.1 for tributaries with no detections. However, these estimates resulted in much higher loadings than those calculated using half the detection limits. These estimates must be overestimates since the expected concentrations derived from the partitioning calculations would have resulted in detectable concentrations in the water samples. The concentrations predicted by the partition coefficients are most likely high because they do not take into account other mitigating factors, such as dissolved organic carbon, carbon quality, and disequilibria within the water column. Therefore, the half detection limit basis was used in estimating the load.

The total average annual loading of the BTEX compounds to Onondaga Lake via tributaries was estimated to be on the order of 1,200 kg/yr, with approximately equal contributions from each of the compounds (Table 6-33). Onondaga Creek and Ninemile Creek make up approximately 60 percent of the total tributary loading, with about 360 kg/yr from Ninemile Creek and about 380 kg/yr from Onondaga Creek. However, both of these estimates are based solely on using half the detection limits to estimate concentrations, since all of the samples collected in these two creeks were reported as less than the detection limit. Thus, the relatively high estimated loads are the result of the large contribution of these streams to the total tributary flow into the lake, and not their associated contamination.

The estimates for Sawmill Creek and Bloody Brook (16 and 60 kg/yr, respectively) were also based solely on half the detection limits. Of the 1,200 kg/yr of BTEX loads estimated by this analysis, only about 150 kg/yr are based on actual detections in the water column of the tributaries; specifically, the East Flume, Harbor Brook, Ley Creek, and Tributary 5A, as well as Metro. The highest single flux exclusive of nondetects was for Metro effluent, which had an annual loading of toluene on the order of 68 kg/yr. No other BTEX compounds were detected in the Metro discharge.

Groundwater Advection

Groundwater data as reported in the Semet Residue Ponds RI (O'Brien & Gere, 1991), Willis Avenue RI (O'Brien & Gere, 2002e, under revision), and the recent pumping tests report (O'Brien & Gere, 2002f) from wells along the lakeshore were used to estimate annual BTEX groundwater advection loading to Onondaga Lake. Details of this calculation and the models used to calculate groundwater flux to the lake are discussed in Sections 6.1.1.3 and 6.2.1. With the use of these models, it was estimated that groundwater flow into the lake contributes BTEX compounds on the order of 9,300 kg/yr from the Willis Avenue, Semet Residue Ponds, and Wastebed B/Harbor Brook sites (Table 6-34). Approximately 65 percent and 28 percent of this input originates from the Willis Avenue and Semet Residue Ponds sites, respectively, through the sand and gravel hydrogeologic unit.

Of the BTEX compounds, benzene makes up approximately 68 percent of the total loadings, at about 6,300 kg/yr. Toluene is the next largest flux at 2,500 kg/yr, 27 percent of the total. Ethylbenzene and xylenes make up only about 1 and 4 percent, respectively. The contribution from the I-690 drainage system, included in the loading estimate, was on the order of 80 kg/yr. Approximately 84 percent of this was benzene (Table 6-35).

Flux from Sediment Porewater

Average annual loadings of BTEX compounds to Onondaga Lake via porewater diffusion were estimated using average surface sediment concentrations from the profundal and littoral zones in Onondaga Lake. The appropriate organic/water partition coefficients were applied to the sediment concentrations, assuming 10°C for the profundal zone and 20°C for the littoral zone. The average annual loading of BTEX compounds through porewater diffusion to Onondaga Lake was estimated to be on the order of 750 kg/yr (Table 6-35). Approximately 78 percent of this input is due to porewater diffusion in the littoral zone.

Loadings of BTEX compounds to Onondaga Lake via porewater advection were estimated separately for the littoral zone in front of Wastebed B/Harbor Brook and the Willis Avenue/Semet Residue Ponds areas using the average surface sediment concentrations (0 to 2 cm) and the equilibrium partitioning model described in Section 6.2.1. Total loadings were estimated to be on the order of 210 kg/yr, with approximately 68 percent of this from the Wastebed B/Harbor Brook area. About 65 percent of the Wastebed B/Harbor Brook area contribution was from xylene. Of the estimated 67 kg/yr contribution from the Willis Avenue/Semet Residue Ponds area, approximately 72 percent was benzene. These fluxes are relatively minor in comparison to the estimates for groundwater advection in the littoral zone area between Tributary 5A and Harbor Brook.

Precipitation

No data were found for concentrations of BTEX compounds in rainfall. In order to get an estimate of the potential annual loading due to rainfall, the Henry's Law constants were applied to urban ambient air concentrations reported by ATSDR (1995a, 1997b, 1999c, and 2000b), as described in Section 6.2.1. Using rainfall data from 1992 (NOAA, 1992), the annual loading of total BTEX compounds via rainfall was estimated to be on the order of 0.5 kg/yr (Table 6-35). Approximately 47 percent of this was xylenes. As would be expected, loadings through rainfall are insignificant. This is most likely due to the tendency of the compounds to partition into the air phase.

In-Lake Resuspension

Resuspension of contaminated sediments can contribute to contamination within the water column. A model was developed for mercury to estimate the loadings due to resuspension over the stratified period. A detailed discussion of this model can be found in Section 6.1.3. For this discussion, this model was applied to area-weighted average surface sediment concentrations from the 0 to 2 cm interval, as discussed in Section 6.2.1, to estimate the average BTEX loadings to Onondaga Lake over the stratified period via resuspension. Total BTEX loadings to the lake over the stratified period are estimated to be on the order of 36 kg, with approximately 83 percent of this input from xylenes (Table 6-35). The inputs of the other BTEX compounds, which comprise the remaining 17 percent, are all of the same order-of-magnitude.
6.2.3.3 Losses from Onondaga Lake

Volatilization

As previously discussed, BTEX compounds are volatile, and the most common mechanism for loss from surface water is through volatilization. Using surface water samples collected in 1999 from Onondaga Lake and assuming the ambient concentrations to be zero for the upper-bound estimate, a volatilization rate was calculated for each of the BTEX compounds (Table 6-36). This method of calculation is discussed in detail in Section 6.1.2. The total loss of BTEX compounds from the lake surface was estimated to be on the order of 2,500 kg/yr, with the following breakdown: approximately 1,300 kg/yr benzene, 250 kg/yr toluene, 487 kg/yr ethylbenzene, and 487 kg/yr total xylenes. It should be noted that the ethylbenzene flux was based solely on non-detects. Toluene and xylenes are each based on one nearshore detection.

Outflow

BTEX compounds were not detected in surface water samples collected in 1992 and 1999 from 0 to 3 m in the center of the northern basin of the lake, indicating that these compounds were not discharged from the lake via surface water discharge at a measurable rate. Rather, volatilization across the lake surface, degradation, and deposition with particles to the sediment column are more likely mechanisms responsible for removing the compounds from the water column. However, for the purpose of estimating a potential annual average load, half the detection limits were used to estimate the concentrations, as discussed in Section 6.2.1. It was estimated that BTEX compounds could be released from the lake via surface water on the order of 800 kg/yr (Table 6-36). It should again be noted that this estimation is based solely on half the detection limits and, therefore, may overestimate the value.

Particle Settling

In order to estimate BTEX loading to the lake sediments from the lake water column via particle settling, the estimated BTEX concentration in suspended sediments was multiplied by the particle flux rate measured from the sediment trap data, as discussed in Section 6.2.1. Because there were no detectable concentrations of BTEX in the lake surface water samples from either of the deep basin stations, the average concentrations from the surface sediment in the littoral zone near the Honeywell sites were used to estimate the concentrations on the suspended particles. A particle load of 9.7×10^6 kg was estimated for the stratification period, as discussed in Section 6.1.2. The estimated loss of total BTEX compounds to Onondaga Lake sediments via particle settling is on the order of 26 kg for the stratified period, with about 50 percent coming from xylenes (Table 6-36).

6.2.3.4 In-Lake Processes

Of the processes and estimates discussed above, groundwater advection dominates BTEX inputs to Onondaga Lake (80 percent of the estimated loads), with benzene being the most abundant of the compounds entering the lake. Tributaries and porewater diffusion contribute smaller (approximately 10

percent each) but significant inputs of BTEX, although the tributary estimates are likely high due to the infrequency of detections. This is consistent with what would be expected, based on the behavior of BTEX compounds. Within the water column, the compounds would be available for volatilization and degradation. Within the groundwater, volatilization would be limited to available pore space.

As previously discussed, the largest mechanism controlling fate of BTEX compounds in the water column is volatilization from surface water, accounting for 75 percent of the estimated losses. Flow out of the lake accounts for 24 percent and settling to the lake bottom contributes approximately 1 percent, and these estimates are both likely high. Microbial degradation and photooxidation may also remove BTEX compounds from the lake; however, no data are available to estimate losses by these mechanisms accurately.

6.2.3.5 In-Lake Distribution and Likely Sources

As discussed in Chapter 5 and presented in Figures 5-10 through 5-14, BTEX compounds were detected at the highest concentrations in the littoral zone in the area extending from Harbor Brook to Wastebeds 1 through 8. Based on the loading calculations, the primary source of current BTEX contamination to the lake is via groundwater through the Willis Avenue and Semet Residue Ponds sites (Table 6-34). There was also a contribution from groundwater from the Wastebed B/Harbor Brook site, but it was only approximately 7 percent of the loadings from Willis and Semet. While the Wastebed B/Harbor Brook site may be a less significant source of BTEX compounds (investigation is ongoing), high levels of BTEX expand out from the area, indicating that the in-lake waste deposit is also a likely source of BTEX loads to the lake.

In summary, the primary source of BTEX to the lake is via groundwater originating on the Willis Avenue and Semet Residue Ponds sites, as well as the Wastebed B/Harbor Brook site. Porewater diffusion and the Honeywell in-lake waste deposit are also likely sources. The primary loss of BTEX from the lake appears to be via volatilization. However, like many of the fluxes for BTEX, this estimate is hampered by the lack of detectable concentrations in lake media. Nonetheless, this loss term is consistent with the geochemical nature of this relatively volatile group. Although it cannot be directly estimated here, losses via microbial degradation and photolysis are also likely for this group and probably represent a significant sink for BTEX. Overall, inputs of BTEX to the lake appear quite large (on the order of 11,000 kg/yr), but the estimates of both inputs and losses are hampered by the limited sensitivity of the available data.

6.2.4 Chlorinated Benzenes

This section discusses the fate and transport of chlorinated benzene compounds (chlorobenzene, dichlorobenzenes, trichlorobenzenes, and hexachlorobenzene) in Onondaga Lake. Chlorinated benzenes were produced by the Honeywell plant that was in operation from 1918 until 1977. Sources of chlorinated benzenes and other CPOIs are described in Chapter 4.

6.2.4.1 Environmental Persistence and Fate

The aqueous solubility of chlorobenzene is approximately 500 mg/L, and solubility decreases with each additional chlorine substitution. Hexachlorobenzene, for instance, has an aqueous solubility of 0.006 mg/L. Due to the relatively low aqueous solubility (and correlated high lipophilicity) of chlorinated benzenes, these compounds tend to bind and remain associated with the natural organic matter in Onondaga Lake sediments. The low occurrence of chlorinated benzenes in water samples reflects this tendency to remain associated with sediment. The less chlorinated forms are also fairly volatile, further reducing their concentrations in lake water. Regarding environmental persistence, degradation of chlorinated benzenes tends to occur by dechlorinated benzenes more persistent in the environment. The most recalcitrant of the chlorinated benzenes, hexachlorobenzene, is likely to reside in the environment for time periods on the order of decades, whereas less substituted rings will degrade somewhat faster.

6.2.4.2 Inputs to Onondaga Lake

Tributary Loads

The inputs of chlorinated benzenes from tributaries to Onondaga Lake were estimated using the data collected in 1991 and 1992. The loads were estimated using the surface water concentrations and the average annual flow for each tributary, as discussed in Section 6.2.1. Due to the low aqueous solubility of chlorinated benzenes, their input to the lake from the tributaries is expected to be relatively minor. The loadings of chlorinated benzenes from the tributaries to the lake, which are presented in Table 6-37, are summarized as follows:

- Chlorobenzene was only detected in the East Flume. The input of chlorobenzene from the East Flume was estimated at 2 kg/yr.
- Dichlorobenzenes were detected in Tributary 5A, Harbor Brook, and the East Flume. The loads from the East Flume and Harbor Brook are on the same orderof-magnitude, with values of 29 and 22 kg/yr, respectively. Dichlorobenzenes input from Tributary 5A were estimated at only 5 kg/yr. This is due to the detection of a single isomer, 1,4-dichlorobenzene, being found in the surface water collected in 1991. Two forms were detected in Harbor Brook: 1,2- and 1,4- dichlorobenzene. In the East Flume, all three isomers were found.
- Trichlorobenzenes were only detected in the East Flume, with a load of 5 kg/yr.
- Hexachlorobenzene was not detected in any of the tributaries waters, and was detected only in the surface sediments of Ninemile Creek collected in 1998 and 2001. Using the sediment concentrations at Ninemile Creek, the loading of

hexachlorobenzene is estimated at 20 kg/yr. No loadings of hexachlorobenzene were estimated for the other tributaries.

The sediment concentrations were used to estimate an alternate loading value whenever there were frequent non-detect results in the water samples. The equilibrium-based equation used to obtain the concentration in the water column from the sediment concentration is discussed in Section 6.2.1. In all cases, the equilibrium-based model concentrations were higher than the measured value or reported detection limit of the water column samples, except for dichlorobenzenes in Onondaga Creek. With this exception, the loadings of chlorinated benzenes from the tributaries were calculated based on half of the detection limit, yielding a result that is probably an upper-bound estimate of the actual load. The loadings of chlorinated benzenes ranged from 2 to about 250 kg/yr (see Table 6-37).

Groundwater Advection

This section presents the loadings of chlorinated benzenes to the lake via groundwater advection in front of the Willis Avenue, Semet Residue Ponds, and Wastebed B/Harbor Brook sites. The estimation of the input of chlorinated benzenes via groundwater advection is based on the conceptual model of groundwater from upland sites moving through preferred pathways, not chemically interacting with the sediments. The groundwater flow rate estimation and monitoring wells used for the contaminant concentrations are discussed in Section 6.1.1.3. The loadings of chlorinated benzenes to the lake via groundwater, which are presented in Table 6-38, are summarized as follows:

- The chlorobenzene load from the Honeywell lakeshore area was estimated to be on the order of 3,000 kg/yr, with approximately 96 percent of the loading from the Willis Avenue site. The hydrogeologic units of the aquifer at the Willis Avenue site that contribute the largest loads to the lake are the shallow and the deep layers; i.e, the fill unit and the sand and gravel unit. The contributions of chlorobenzene from the fill unit and the sand and gravel unit were estimated at about 1,000 and 1,900 kg/yr, respectively.
 - The dichlorobenzenes load via groundwater was estimated to be on the order of 3,700 kg/yr, with the majority of the loading again coming from the Willis Avenue site (93 percent). Similar to chlorobenzene, dichlorobenzenes were found in the deep hydrogeologic unit at the Willis Avenue site. For dichlorobenzenes, the fill unit contributes about 800 kg/yr and the sand and gravel unit contributes about 2,600 kg/yr.

The contribution of dichlorobenzenes from the Semet Residue Ponds area was estimated at 13 kg/yr. Dichlorobenzenes in the Wastebed B/Harbor Brook area were estimated at 260 kg/yr. It should be noted that the concentration in the Wastebed B/Harbor Brook monitoring Well HB-1S (4,600 μ g/L) was much

higher than the other wells on the site. The concentrations in Well HB-1S caused the average dichlorobenzenes concentration to rise from about 400 to 1,500 μ g/L.

- Trichlorobenzenes loading to the lake via groundwater was less significant than the chlorobenzene and dichlorobenzenes loadings. The total loading of trichlorobenzenes was estimated at about 90 kg/yr.
- No hexachlorobenzene loading was reported since there was no detection in any of the wells.

As noted in Section 6.1.1.3, there is a storm drain system for the segment of I-690 that runs through the Willis Avenue and the Semet Residue Ponds sites. Chlorobenzene, dichlorobenzenes, and trichlorobenzenes were detected at Outfall 41. Table 6-39 shows the estimated loading of chlorinated benzenes from the outfall. Chlorobenzene and dichlorobenzenes inputs via the I-690 drains were each about 220 kg/yr, and inputs of trichlorobenzenes were less than 1 kg/yr.

Flux from Sediment Porewater

In addition to the groundwater loads described above, loadings of chlorinated benzenes to the lake using surface sediment concentrations were also estimated. In this conceptual model, it was assumed that groundwater discharges uniformly across the littoral zone's ediments and displaces sediment porewater upward into the epilimnion by displacement. The surface sediment concentrations (0 to 2 cm) were used to estimate the porewater concentrations by applying the formula presented in Section 6.2.1.

These loadings were estimated due to a concern that the porewater advection might create large fluxes of chlorinated benzenes to the lake. However, the calculations indicated that the values were much lower than those of the groundwater advection. The estimated chlorinated benzenes loading using porewater concentrations are included in Table 6-39. Chlorobenzene loading was approximately 100 kg/yr, while dichlorobenzenes were approximately 30 kg/yr. Trichlorobenzenes loading was on the order of 2 kg/yr and hexachlorobenzene loading was insignificant, with a value on the order of 0.015 kg/yr.

Another mechanism that may bring the surface sediment concentrations to the water column is diffusion. In this instance, the concentration gradient between the sediment and the overlying water causes the contaminant to migrate through the porewater to the water column. The concentrations were again estimated using the method described in Section 6.2.1, assuming the system is in equilibrium. From these estimations, it appears that diffusion from the littoral zone may be an important mechanism for chlorobenzene release. Chlorobenzene input to the water column was estimated to be about 250 kg/yr (Table 6-39). Diffusion flux is a less important mechanism for dichlorobenzenes, giving an input of approximately 90 kg/yr to the lake. This mechanism yielded smaller fluxes for trichlorobenzenes and hexachlorobenzene.

The diffusion flux of the chlorinated benzenes from the profundal zone was also estimated. Chlorinated benzenes loading from the profundal zone was relatively minor, with values ranging from 0.01 to 11 kg (see Table 6-39).

Dense Non Aqueous Phase Liquid

Sampling and active recovery have confirmed that pools of chlorinated benzenes DNAPL in the subsurface exist near the shoreline of the Honeywell Willis Avenue site. This DNAPL certainly acts as a source of chlorinated benzenes to the groundwater, and explains why such high concentrations have been detected in groundwater. Based on sediment sampling, it is believed that the DNAPL is migrating and reaching the lake. Therefore, since the loading calculations are based on concentrations present in the groundwater (DNAPLs were not included) the actual loading of chlorinated benzenes to the lake is likely to be much higher than estimated.

Precipitation

The input of chlorinated benzenes to Onondaga Lake via precipitation to the lake surface was estimated from rainfall rates, the surface area of the lake, and assumed concentrations of chlorinated benzenes in air. A total volume of 1.33×10^7 m³ of precipitation was estimated based on the annual precipitation in the Syracuse area for the year 1992 (NOAA, 1992), as discussed in Section 6.2.1.

Since only air concentrations were available for the chlorinated benzenes, the concentrations of chlorinated benzenes in the aqueous phase were obtained using the air-water equilibrium model. The equation used to calculate the fraction in the vapor phase is presented in Section 6.2.1.

The chlorinated benzenes input via precipitation appears to be insignificant. The average concentration of chlorobenzene in precipitation was $19,000 \text{ ng/m}^3$. This concentration gives an estimate of 0.26 kg/yr of chlorobenzene input to the lake surface from precipitation. Dichlorobenzene and hexachlorobenzene input to the lake were only about 0.05 and 0.09 kg/yr. There were no data available to estimate trichlorobenzene input to the lake, but it is unlikely that this precipitation flux is important for this contaminant. Table 6-39 summarizes the loadings of chlorinated benzenes via precipitation.

In-Lake Resuspension

Resuspension of contaminated sediments in the in-lake deposit area contributes contamination to the lake. A model was developed based on the relationship between wind conditions and resuspension. Details of the model used to calculate the loadings due to resuspension can be found in Section 6.1.3.

For chlorinated benzenes, the model was applied using the area-weighted average surface sediment concentrations in the in-lake waste deposit over the stratified period (120 days). Chlorobenzene loading to the lake due to resuspension was on the order of 90 kg/yr. Similarly, dichlorobenzenes loading was on

the order of 54 kg/yr. Loadings of trichlorobenzenes and hexachlorobenzene were on the order of 6 and 0.7 kg/yr, respectively. The estimated values are presented in Table 6-39.

6.2.4.3 Losses from Onondaga Lake

Volatilization

Volatilization from the lake was calculated using the chlorinated benzenes surface water samples collected at 0 m in the deep basins and nearshore areas. The method of calculation is described in Section 6.1.2. Only chlorobenzene, 1,2-dichlorobenzene, and 1,4-dichlorobenzene were detected in the surface water. The loss of chlorinated benzenes due to volatilization was calculated by taking into consideration the ambient air concentrations, whenever possible. The loss estimate was also modified to account for the part of the year (three months) when the lake is covered with ice and no volatilization occurs.

As for the non-detected trichlorobenzenes, the loss was estimated based on half of the detection limit. This estimation serves as an upper bound. Table 6-40 shows the estimated volatilization fluxes for chlorinated benzenes from the lake. Chlorobenzene volatilizes the most, with an estimated value of approximately 90 kg for the year. Dichlorobenzenes volatilize at a rate of approximately 60 kg. Trichlorobenzenes were not detected in the water column; however, half the detected limit was used to estimate the volatilization. The estimated rate was very small, on the order of 6 kg. Hexachlorobenzene was not analyzed in the surface water (0 m), and it was not detected at depth (6 m). The volatilization of hexachlorobenzene is expected to be even smaller based on its higher K_{oc} value, lower Henry's Law constant, and lower concentrations compared to trichlorobenzenes.

Outflow

Discharge from the lake was calculated using the tributary inflows and the water concentrations for chlorinated benzenes in the 0 to 3 m depth interval of the northern deep basin station. Most chlorinated benzenes were not detected, except for 1,4-dichlorobenzene with a value of $0.15 \mu g/L$. The discharge for dichlorobenzenes was relatively minor, with a value about 80 kg/yr (see Table 6-40). Chlorobenzene was not detected in the water column at this station, but was detected in the sediment. Using the sediment concentrations and the equilibrium model described in Section 6.2.1, the estimated average water concentration was $1.4 \mu g/L$. This value is higher than the detection limit in the water column. Therefore, based on the presence of chlorobenzene in the sediments and its non-detect results in the water column, an upper-bound chlorobenzene discharge (approximately 270 kg/yr) was estimated using half of the detection limit.

No discharge loading for trichlorobenzenes was estimated since there were no detections in near-surface water and surface sediment in the northern basin. Hexachlorobenzene was detected in the sediment in the northern basin, and the concentration in the surface water was estimated using the equilibrium model equation. The discharge rate for hexachlorobenzene using this assumption was estimated at 2 kg/yr.

Particle Settling

The lake sedimentation of chlorinated benzenes from the water column to the profundal zone was calculated based on the measurement of the sediment traps during the stratification period, as discussed in Section 6.1.2. The amount of chlorinated benzenes entering the profundal zone was estimated to be small. For the stratification period, there were only approximately 8 kg each for chlorobenzene and dichlorobenzenes via settling to the profundal zone (see Table 6-40). Trichlorobenzenes and hexachlorobenzene settling-rate fluxes were approximately 1 and 0.09 kg for the stratification period, respectively.

6.2.4.4 In-Lake Processes

Chlorobenzene

Chlorobenzene is fairly volatile, and most of it will be lost to the atmosphere due to evaporation. The rate of evaporation will depend on the wind speed and water movement. The half-life for evaporation is approximately 4.5 hours with moderate wind speed. Biodegradation occurs during the warmer seasons and proceeds more rapidly in fresh water than in estuarine and marine systems. The degradation rate will also depend on the acclimation of microbial communities to chlorobenzene or related chemicals. A moderate amount of adsorption will occur onto organic sediments (ATSDR, 1990).

Dichlorobenzenes

Dichlorobenzenes generally adsorb moderately to tightly onto soils of high carbon content and do not tend to leach into groundwater. In soils, the compound biodegrades slowly under aerobic conditions. In water, the major removal processes are likely to be adsorption onto sediments and bioaccumulation in aquatic organisms. Evaporation from surface water may also be important, but not aquatic hydrolysis, oxidation, or direct photolysis. Dichlorobenzenes may biodegrade in aerobic water after microbial adaptation. They typically do not biodegrade under the anaerobic conditions that may exist in the lake sediments or various groundwaters (ATSDR, 1998a).

1,2-Dichlorobenzene has a high affinity for lipophilic materials and is reported to have a relatively low vapor pressure and low aqueous solubility at ambient temperatures. Sorption, bioaccumulation, and volatilization are competing processes, and the rate at which each of these processes occurs will determine which fate is predominant for 1,2-dichlorobenzene in the aquatic environment. Should volatilization occur at a more rapid rate than sorption or bioaccumulation, then atmospheric processes would be expected to regulate the fate of 1,2-dichlorobenzene. On the other hand, should sorption and bioaccumulation occur more rapidly than volatilization, biodegradation of 1,2-dichlorobenzene by aquatic microorganisms would be anticipated to regulate the fate of this compound (ATSDR, 1998a).

1,4-Dichlorobenzene is a solid that sublimes readily at room temperature. Therefore, 1,4-dichlorobenzene tends to volatilize to the atmosphere from soil and water at a relatively rapid rate. The estimated volatilization half-life in a model river was 4.3 hours (Howard, 1989) and reported volatilization half-lives

in coastal seawater ranged from 10 to 18 days (Wakeham et al., 1983). Volatilization from surface soil may be an important transport mechanism for 1,4-dichlorobenzene (Wang and Jones, 1994), but adsorption to soil particulates may inhibit volatilization by an order-of-magnitude compared to volatilization from water (Wilson et al., 1981). Since 1,4-dichlorobenzene is slightly soluble (79 ppm at 2.5°C) in water (Verschueren, 1983), partitioning to clouds, rain, or surface water may occur. The Henry's Law constant value, 1.5×10^{-3} atm-m³/mol at 20°C (Howard, 1989), indicates that partitioning from air to water is likely to be minor, relative to the reverse process of volatilization of the compound from water to air. However, this compound has been detected in six of seven rainwater samples collected in Portland, Oregon at concentrations ranging from 3 to 7 ng/L (Ligocki et al. 1985).

Based on measured soil organic carbon partition coefficient (K_{∞}) values, which range from 275 to 1,833 in different soils (Bahnick and Doucette, 1988; Newsom, 1985; Schwarzenbach and Westall, 1981; Wilson et al., 1981), 1,4-dichlorobenzene is expected to sorb moderately to soils and sediments. Sorption is primarily to the soil organic phase (Chiou et al., 1983) and, therefore, depends upon the organic content of the soil. However, sorption is likely to be reversible; therefore, 1,4-dichlorobenzene may leach from hazardous waste sites and be transported to groundwater, or may migrate from surface water through the soil to groundwater (Newsom, 1985; Schwarzenbach and Westall, 1981). 1,4-Dichlorobenzene is expected to bioconcentrate in aquatic organisms.

Trichlorobenzenes

Trichlorobenzenes are expected to adsorb onto soils of high organic content, but not leach appreciably into groundwater. They are not hydrolyzed and are unlikely to biodegrade significantly. Some evaporation may occur from soil surfaces. In water, trichlorobenzenes are likely to adsorb onto sediments and bioconcentrate in aquatic organisms. Evaporation from water may be a significant removal process (Spectrum Chemical Fact Sheet, 2002).

1,2,3-Trichlorobenzene (1,2,3-TCB) has been shown to slowly degrade in soil. If released into water, 1,2,3-TCB is expected to adsorb onto the sediment and particulate matter, and to bioconcentrate in aquatic organisms. This compound should not readily biodegrade in water, will not hydrolyze (estimated half-life of 4.9 yr), and should not undergo degradation by direct photolysis. Volatilization into the atmosphere should be rapid (Spectrum Chemical Fact Sheet, 2002).

1,2,4-Trichlorobenzene (1,2,4-TCB) is expected to adsorb to the organic matter in soil and, therefore, should not leach appreciably to the groundwater. However, 1,2,4-TCB has been detected in some groundwater samples, which indicates that it can be transported there by some process. It will not hydrolyze but may biodegrade slowly in the soil, based upon the data from one experiment (Spectrum Chemical Fact Sheet, 2002). It is not expected to biodegrade in groundwater. Sorption of 1,2,4-TCB to a series of subsurface soil samples has been reported. Desorption of sorbate from the sorbent matrix provides better precision than conventional solution-phase concentration differences when sorption is low. Clay mineral content influences sorption on low-carbon sorbents. If 1,2,4-TCB is released to water it will be expected to adsorb to the sediment. Adsorption to sediments or absorption by microorganisms may

minimize the evaporation process. It is not expected to appreciably directly photolyze in surface waters based on a reported half-life for sunlight photolysis in surface water at 40 degrees latitude in summer. Half-lives ranging from 1.5 to 28 days were estimated in rivers in the Netherlands, based upon monitoring data (Spectrum Chemical Fact Sheet, 2002).

Hexachlorobenzene

Hexachlorobenzene has a moderate vapor pressure and has a very low solubility in water. If released to the atmosphere, hexachlorobenzene can exist in the vapor phase in association with particulates. Although physical removal of hexachlorobenzene from the atmosphere is possible via both wet and dry deposition (Howard, 1989), the compound is hydrophobic and somewhat resistant to wet deposition scouring unless it becomes sorbed to airborne dust or cloud condensation nuclei. Hexachlorobenzene photolyzes slowly in the atmosphere and has a half-life of about 80 days. The main chemical reaction in water is slow photolysis, whereas hydrolysis and oxidation appear to be unimportant. Biotransformation of hexachlorobenzene in surface water, sludge, or soil suspension is extremely low (ATSDR, 2002).

The Henry's Law value for this compound suggests that releases of hexachlorobenzene to surface water will volatilize at a moderate rate, and that volatilization can be a significant transfer mechanism (Thomas, 1990). If released to water, adsorption of hexachlorobenzene to sediment or soil particulates is also expected to be significant on the basis of the high organic carbon partition coefficient (K_{oc}) value (USEPA,1981). Since hexachlorobenzene will adsorb strongly to soil particles and sediments, it may build up in the bottom sediments of large aquatic systems.

The high octanol/water partition coefficient (K_{ow}) value for hexachlorobenzene suggests that bioconcentration and biomagnification of hexachlorobenzene are likely to occur to a significant degree.

6.2.4.5 In-Lake Distribution and Likely Sources

As presented in Chapter 5 (Figures 5-15 through 5-19), chlorinated benzenes in sediments are concentrated in the southernmost quarter of Onondaga Lake, particularly along the southwestern shore. The highest concentrations were measured generally between 15 and 100 cm below the surface. These observed sediment distributions are consistent with chlorinated benzenes entering with waste discharges from the East Flume, surface water, and groundwater in the Willis Avenue area. However, the occurrence of chlorinated benzenes at depth suggests disposal of Honeywell waste directly into the lake near Harbor Brook and the East Flume. Elevated dichlorobenzene concentrations extend to a depth of 6 to 7 m near the mouth of Harbor Brook, while elevated chlorobenzene and hexachlorobenzene concentrations extend to a depth of 7 to 8 m near the East Flume. Furthermore, chlorinated benzenes in DNAPL form are found immediately next to the shoreline on the Honeywell property, and DNAPL was observed in the lake sediments during installation of piezometers in front of the Honeywell property in November 2002. Detection of chlorobenzene in surface water near the Willis Avenue site is consistent with an ongoing source of chlorobenzene to the water column.

In summary, the largest source of chlorinated benzenes to the lake is via groundwater advection from the Willis Avenue site, which is at least an order-of-magnitude greater than any other source of contamination. The largest loss mechanism is likely volatilization, although lake discharge may be important as well. Notably, the estimate of groundwater transport is more than an order-of-magnitude greater than the combined losses via volatilization and lake discharge. This large discrepancy suggests either a large unknown sink or a large error in one or more flux estimates. One possible missing sink may be direct adsorption of chlorinated benzenes within the sediments of the lake bottom. Such a scenario would leave the water column relatively free of chlorobenzene contamination but would extensively contaminate the sediments near the groundwater discharge, as has been observed.

6.2.5 Polycyclic Aromatic Hydrocarbons

This section discusses the fate and transport of PAHs in Onondaga Lake. In the following discussion, the PAH compounds are sometimes separated into two groups: low molecular weight PAHs (LPAHs) and high molecular weight PAHs (HPAHs). These two groups represent the entire suite of 17 PAH compounds reported.

6.2.5.1 Environmental Persistence and Fate

PAHs enter the environment mostly as releases to air from volcanoes, forest fires, residential wood burning, and exhaust from automobiles and trucks. They can also enter surface water through discharges from industrial plants, such as the Honeywell facilities and wastewater treatment plants, and they can be released to soils at hazardous waste sites if they escape from storage containers. PAHs were produced by the Honeywell plant in conjunction with the benzene, toluene, and xylenes product line. In addition, Honeywell industrial wastes were discharged into the lake (e.g., via the East Flume; see Chapter 4, Section 4.5.1) and these deposits contain PAHs. Oil City, an area alongside Onondaga Creek that was formerly a bulk storage area for various petroleum products, was also a potential sources of PAHs. The movement of PAHs in the environment depends on properties such as how easily they dissolve and evaporate (ATSDR, 1995b).

PAH compounds tend to be removed from the water column by volatilization to the atmosphere, by binding to suspended particles or sediments, by being accumulated or sorbed onto aquatic biota, or by degradation. LPAHs are more susceptible to volatilization as they have a relatively high Henry's Law constant. Because of low solubility and high lipophilicity, LPAHs in aquatic systems are primarily found sorbed to particles that either have settled to the bottom or are suspended in the water column. HPAHs have stronger tendencies to adsorb to organic carbon than LPAHs. The majority of HPAHs are expected to remain bound to sediment and, at the degradation rates typical of that anaerobic environment, they are likely to persist for a few decades.

6.2.5.2 Inputs to Onondaga Lake

Tributary Loads

The tributary PAH loads were estimated using the method discussed in Section 6.2.1. Surface water samples were collected and analyzed for PAHs by NYSDEC at Harbor Brook, Ley Creek, and Onondaga Creek in 1996 and 1997 sampling events. From seven samples collected in Harbor Brook, naphthalene was detected in three samples and acenaphthene was detected in two samples. Other detected PAHs from Harbor Brook samples include 2-methylnaphthalene, acenaphthylene, fluorene, and phenanthrene, although each of them was detected only once. For the two samples collected at Ley Creek and one sample at Onondaga Creek, none of the PAHs were detected with a detection limit of 10 μ g/L. These data indicate that Harbor Brook contains the highest surface water concentrations of PAHs relative to the other tributaries. The average concentrations and USGS annual flow are used to calculate the annual loads from Harbor Brook. Naphthalene has the highest annual load, at about 170 kg/yr. The loads of other detected PAHs in Harbor Brook range from 20 to 60 kg/yr (Table 6-41).

Twenty-four samples from four stations were collected by Exponent at Ninemile Creek and Geddes Brook in 1998. None of these samples had detectable concentrations of PAHs. These data suggest that Ninemile Creek and Geddes Brook do not contribute significant amounts of PAHs to the lake.

Sediment data were used to estimate the tributary loads, as discussed in Section 6.2.1. The discussion to follow is based on these equilibrium-partitioning model-based loads. For Harbor Brook, which had detected concentrations in surface water, loads estimated from sediments were compared with loads estimated from surface water concentrations.

Of all the tributaries, Harbor Brook has the highest sediment PAH concentration. The East Flume, Bloody Brook, and Sawmill Creek have the same range of PAH concentrations as Ninemile Creek (a few hundred $\mu g/kg$). PAH concentrations at Tributary 5A range from a few hundred to a few thousand $\mu g/kg$. Ley Creek and Onondaga Creek have higher concentrations than the other stations, but these are still two to three times lower than the concentrations at Harbor Brook.

As shown in Table 6-41, the naphthalene load estimated for Harbor Brook using the sediment data (78 kg/yr) is lower than the load estimated using surface water concentrations (167 kg/yr), while for acenaphthylene, the load based on the sediment data (67 kg/yr) is higher than load based on water data (22 kg/yr). The comparison of the two methods of estimating load suggests that they agree within a factor of two and that the equilibrium model results are acceptable, when needed, for an order-of-magnitude estimate of tributary load. For most PAHs in Ninemile Creek, Tributary 5A, East Flume, Bloody Brook, and Sawmill Creek (with the exception of acenaphthylene), the model-estimated load is less than 5 kg/yr. This suggests that the contribution of these PAHs from these tributaries may be relatively unimportant to the lake's PAH budget (Table 6-42).

Loads at Ley Creek range from 1 kg/yr for dibenz(a,h)anthracene to 95 kg/yr for acenaphthylene. When studying the source of PAH contamination in the lake, Hubbard (1996) concluded that Ley Creek is not a major source of PAHs because the concentration of pyrene in Onondaga Lake near the mouth of Ley Creek is usually equal to or greater than concentration found in Ley Creek itself. Due to the high flow rate and relatively low TOC value, loads from Onondaga Creek are greater than the loads at Ley Creek, which has much lower flows (Table 6-42). Among all the PAHs, acenaphthylene has the highest load for all the stations except Harbor Brook. However, this flux may be overestimated due to the unusually low K_w value indicated for this compound. This can be seen from the fact that the flux of this compound (21.5 kg/yr) is roughly one-eighth of that of naphthalene (168 kg/yr) on the basis of the detected water column concentrations in Harbor Brook (Table 6-41). However, the flux of acenaphthylene is equal to that of naphthalene (on the order of 70 kg/yr) for Harbor Brook based on the sediment-based equilibrium partitioning model estimate (Table 6-42). This suggests that the partition coefficient for acenaphthylene may be too low by as much as eightfold. As can be seen in Table 6-42, an eightfold reduction in this coefficient places the acenaphthylene flux within the estimated range of the other PAHs. In further support of this suggestion, among the six PAHs detected in Harbor Brook water, acenaphthylene is the only compound whose sediment-based flux estimate exceeds its water measurement-based estimate.

Groundwater Advection

Groundwater data collected in 1997, 1999, and 2001 from wells along the lakeshore were used to estimate the PAH loads via groundwater advection to Onondaga Lake for the Willis Avenue, Semet Residue Ponds, and Wastebed B/Harbor Brook sites. Details of the model used to calculate groundwater flux to the lake are discussed in Section 6.1.1.3.

Naphthalene has the highest groundwater load, about 530 kg/yr. The loads for other PAHs are on the order of 10 to 50 kg/yr. Loads from the Wastebed B/Harbor Brook site are always higher than the loads from Willis Avenue and Semet Residue Ponds, consistent with the known naphthalene DNAPL plume on the site. For naphthalene, 95 percent of the load comes from the Wastebed B/Harbor Brook site, and the majority of the PAH loads come from the fill layer (Table 6-43).

Based on this analysis, groundwater and DNAPL would appear to be the major external source of PAHs, particularly naphthalene, to the lake.

Flux from Sediment Porewater

The 0 to 2 cm surface sediment concentrations were used to estimate porewater concentrations. Surface sediment data were grouped into six different segments, four in the littoral zone and two in the profundal zone, as described in Section 6.2.1. Average surface sediment concentrations were calculated as the representative concentration for each segment. The appropriate organic/water partition coefficients and average foc value for each segment were applied to the average surface sediment concentration to calculate the porewater concentration as discussed in Section 6.2.1.

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With the highest concentrations in the sediment, naphthalene was chosen from the LPAH group as the representative compound for this calculation. Among HPAHs, fluoranthene has the highest sediment concentration, acenaphthylene has the lowest K_{oc} , and benzo(a)pyrene has the highest toxicity to human health. All three compounds were chosen to represent the HPAH group. As expected, the diffusion load of acenaphthylene is the highest (9,500 kg/yr) due to the low K_{oc} value. The load for acenaphthylene is likely an overestimate since this compound was not detected in lake water samples, which questions the accuracy of the K_{oc} value.

The diffusion load of naphthalene is on the order of 530 kg/yr from the littoral zone and 96 kg/yr from the profundal zone, comparable to its groundwater flux. The diffusion load of fluoranthene is also comparable to its groundwater load, on the order of 20 kg/yr. Benzo(a)pyrene's diffusion load is smaller, which would be expected based on its high K_{∞} value. In general, porewater advection loads are one to two orders-of-magnitude lower than the diffusion load (Table 6-44).

Dense Non-Aqueous Phase Liquid

A pool of PAH DNAPLs exists in the subsurface at the eastern end of the Wastebed B/Harbor Brook site and in sediments of the lower reach of Harbor Brook near the lake. This DNAPL consists mainly of naphthalene and is found primarily on the top of the till layer. The DNAPL acts as a source of PAHs to the groundwater which discharges to Harbor Brook and Onondaga Lake. While the DNAPL may be migrating to the lake, no data exist to quantify the migration rate. If the DNAPL is migrating, the loading of PAHs could be substantially greater than is indicated by the groundwater loading estimates alone. The extent of this DNAPL plume is currently being investigated as part of the RI for the Wastebed B/Harbor Brook site.

Precipitation

The input of PAHs to Onondaga Lake via precipitation to the lake surface was estimated from rainfall rates, as discussed in Section 6.2.1. Data were used from studies on snow cores conducted in northern and central Minnesota and at Eagle Harbor, Michigan on Lake Superior between 1982 and 1992. Relatively low concentrations of total PAHs as the sum of 21 individual PAHs (35 to 120 ng/L) were found at the rural/remote sites. Higher concentration (total PAHs 230 to 3,280 ng/L) were found nearer the urban areas (Franz and Eisenreich, 2000). For individual PAHs, the highest concentration found near the urban area is 610 ng/L. Considering the urban character of Onondaga Lake, the total PAH concentration in precipitation to Onondaga Lake's surface was assumed to be 3,300 ng/L and 600 ng/L for individual PAHs as the highest likely concentrations. Using these concentrations yields an annual flux of approximately 44 kg/yr for total PAHs and a maximum 8 kg/yr for any individual PAH input to the lake surface from precipitation (Table 6-44).

In-Lake Resuspension

The resuspension model described in Section 6.1.3 is used to estimate the load of PAHs from sediment to water column via resuspension from the in-lake waste deposit during the stratified period. The same four

PAHs are included in this estimate as in the porewater diffusion calculations. The 0 to 2 cm surface sediment concentrations for the in-lake waste deposit were averaged and applied to the model. Since the samples are distributed unevenly and could cause some biases, both area-weighted average concentrations and straight average concentrations were used in the calculation. Over the stratified period, the naphthalene loading due to resuspension was on the order of 41 to 55 kg and the fluoranthene loading was on the order of 7 to 17 kg. As mentioned above, naphthalene and fluoranthene have higher sediment concentrations than other PAHs in the same group (LPAHs and HPAHs, respectively). Loading for other PAHs will be lower. As shown in Table 6-44, the load of benzo(a)pyrene is about 1 to 4 kg while acenaphthylene is about 1.5 kg for the period.

6.2.5.3 Losses from Onondaga Lake

Volatilization

Volatilization is considered as one of the major loss processes for organic compounds in lakes (Golightley, 1995). The two-film model described in Section 6.1.2 was used to calculate the PAHs volatilization rate. In Honeywell's 1992 sampling event, PAH concentrations were measured for water samples collected at depths of 6 m and 12 m. All samples were non-detected with the detection limit of 10 μ g/L.

In a previous study (Golightley, 1995), dissolved naphthalene concentration was measured at $0.35 \mu g/L$ in Onondaga Lake. The PISCES results from another study (Hubbard, 1996) indicated that naphthalene concentrations in lake water are on the order of 0.5 to $1 \mu g/L$, and higher than other PAHs. Based on these data, the dissolved naphthalene concentration is assumed to be $0.35 \mu g/L$ in this analysis. Given the information that naphthalene has the highest solubility and the lowest partition coefficient among the PAH compounds (Mackay et al., 1992), and based on observations from other sites such as Lake Michigan (Offenberg et al., 2000) and Chesapeake Bay (Gustafson et al., 1997), it is assumed that the water concentrations of other PAH compounds are all lower than naphthalene. PAH air concentrations in urban areas listed in the literature (ATSDR, 1995b; Gigliotti et al., 2000) range from less than 0.15 to 20 ng/m³. As an upper-bound estimate of the volatilization flux, the concentration in the air was assumed to be zero.

From these assumptions, the volatilization loss of naphthalene is on the order of 406 kg/yr, which defines the upper bound of any individual PAH volatilization loss from the lake (Table 6-45). This estimate represents the maximum loss term for the PAH group.

Outflow

Assuming that volume of the lake is essentially constant, the outflow from the lake will be equal to the inflow from the tributaries and Metro. The sum of tributary flow is about 530×10^6 m³ per yr. No water samples were collected near the lake outlet for PAH analysis. As mentioned in the discussion of volatilization loss, $0.35 \mu g/L$ was used as the surface water dissolved-phase naphthalene concentration in the volatilization estimation.

It is reported that dissolved PAHs accounted for 84 percent of the total PAHs measured in all Lake Michigan water samples (Offenberg et al., 2000). Assuming similar conditions in Onondaga Lake, the water column concentration was estimated to be $0.4 \mu g/L$. As noted in Chapter 5, the northern part of the lake is less contaminated than the southern part. For example, the average concentration measured at the nearshore samples is $0.51 \mu g/L$ for 1,2-dichlorobenzene, while the average concentration for the 0 to 3 m northern deep basin samples is $0.15 \mu g/L$, about threefold less. On this basis, a reduced surface concentration of $0.2 \mu g/L$ was assumed to be a conservative estimate of the naphthalene concentration in the lake's discharge. This yields an annual discharge load of 106 kg/yr (Table 6-45). Also, similar to the volatilization analysis, other PAH surface water concentrations are assumed to be less than naphthalene. Therefore, their loss via lake discharge will be less than 106 kg/yr.

This flux represents a second major loss term for the PAH group. It is smaller than the volatilization estimate but still important. However, as will be discussed later, the loss terms for PAHs do not balance the estimated inputs to the lake.

Particle Settling

PAHs are expected to adsorb very strongly to sediments and particulate matter, especially the HPAH group, which typically has higher K_{∞} values. Therefore, sedimentation is considered to be one of the major loss processes from the water column. However, PAHs were not measured during the sediment trap studies. Instead, the littoral zone 0 to 2 cm surface sediment concentration was applied to estimate the settling flux of PAHs to the lake bottom. With the highest concentration in the littoral zone sediments, fluoranthene had the highest sedimentation loss (70 kg) over the stratification period. The naphthalene loss was about 18 kg. The loads for acenaphthylene and benzo(a)pyrene were relatively small; 6 and 4 kg, respectively (Table 6-45).

6.2.5.4 In-Lake Processes

PAH compounds tend to be removed from the water column by volatilization to the atmosphere, by binding to suspended particles or sediments, by being accumulated by or sorbed onto aquatic biota, or by degradation.

The transport of PAHs from water to the atmosphere via volatilization will depend on the Henry's Law constants (Hs) for these compounds. The LPAHs have Henry's Law constants in the range of 10⁻³ to 10⁻⁵ atm-m³/mol; medium molecular weight PAHs (MPAHs) have constants in the 10⁻⁶ range, and HPAHs have values in the 10⁻⁵ to 10⁻⁸ range. Compounds with values ranging from 10⁻³ to 10⁻⁵ are associated with significant volatilization, while compounds with values less than 10⁻⁵ volatilize from water only to a limited extent. Half-lives for volatilization of benz(a)anthracene and benzo(a)pyrene (HPAHs) from water have been estimated to be greater than 100 hours (ATSDR, 1995b). LPAHs could be substantially removed by volatilization if suitable conditions (high temperature, low depth, high wind) were present. Even for PAHs susceptible to volatilization, other processes, such as adsorption, photolysis, or biodegradation, may become more important than volatilization in slow-moving deep waters, such as Onondaga Lake.

Because of their low solubility and high affinity for organic carbon, PAHs in aquatic systems are primarily found sorbed to particles that either have settled to the bottom or are suspended in the water column. It has been estimated that two-thirds of PAHs in aquatic systems are associated with particles and only about one-third are present in the dissolved form (ATSDR, 1995b). In an estuary, volatilization and adsorption to suspended sediments with subsequent deposition are the primary removal processes for MPAHs and HPAHs, whereas volatilization and biodegradation are the major removal processes for low molecular weight compounds (ATSDR; 1995b).

The LPAHs have a moderate potential to be adsorbed to organic carbon in the sediments. HPAHs have stronger tendencies to adsorb to organic carbon. Sorption of PAHs to sediments increases with increasing organic carbon content and with increasing surface area of the sorbent particles.

The most important processes contributing to the degradation of PAHs in water are photooxidation, chemical oxidation, and biodegradation by aquatic microorganisms (ATSDR, 1995b). Hydrolysis is not considered to be an important degradation process for PAHs. The contribution of the individual processes to the overall fate of a PAH will depend largely on the temperature, depth, pollution status, flow rate, and oxygen content of the water.

The rate and extent of photodegradation vary widely among the PAHs. Based on half-life data, photolysis in water may be an important fate determining process for acenaphthene, acenaphthylene, anthracene, pyrene, benzo(a)pyrene, and benz(a)anthracene relative to the other PAHs. The importance of photolysis will also decrease with the increase of depth in a body of water, particularly in turbid water, because of light attenuation and scattering.

Reactions of PAHs with single oxygen and peroxy radicals are not very important in controlling the overall fate of PAHs in water. PAHs in water can be chemically oxidized by chlorination and ozonation. PAH degradation from chlorination has high efficiency. Pyrene was the most rapidly degraded PAH. Benz(a)anthracene, benzo(a)pyrene, and perylene were also highly degraded. Indeno(1,2,3-cd)pyrene and benzo(g,h,i)pyrene were intermediate with respect to relative degradation. Benzo(k)fluoranthene and fluoranthene were the most slowly degraded of the compounds tested. In water, ozonation is generally slower and less efficient than chlorination in degrading PAHs.

Concentrations of DO greater than 0.7 mg/L are adequate for biotransformation, and the presence of a minimal concentration of PAH is required for biodegradation to proceed (Borden et al., 1989). The minimum total PAH concentration below which biotransformation may be inhibited under ambient nutrient conditions is approximately 30 to 70 μ g/L (Borden et al., 1989). Some other factors that increase the rates of PAH biodegradation are higher water temperature (summer versus winter) and the presence of adapted microorganisms.

Some PAHs are partially or completely degraded by some species of aquatic bacteria and fungi. No correlation between biodegradability and molecular weight is evident in three- to four-ring PAHs. Naphthalene and phenanthrene were reported to biodegrade in water. Other PAHs, such as anthracene,

benz(a)anthracene, chrysene, and fluorene, did not readily biodegrade in water, but degraded readily in sediment-water slurries. On the other hand, PAHs with five or more benzene rings, such as benzo(a)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene, may not biodegrade readily even in sediment-water slurries.

PAHs can be accumulated in aquatic organisms from water, sediments, and food. In fish and crustaceans, biota concentration factors (BCFs) have generally been reported in the range of 10 to 10,000 (ATSDR, 1995b). In general, bioconcentration was greater for the higher molecular weight compounds than for the lower molecular weight compounds.

6.2.5.5 In-Lake Distribution and Likely Sources

This analysis of inputs and outputs suggests that the current major sources of PAHs to Onondaga Lake are groundwater, porewater diffusion, and DNAPL in the area in front of the Honeywell shoreline properties, with lesser amounts due to the tributaries and resuspension of the in-lake waste deposit. The major loss mechanism appears to be volatilization, although biodegradation or photodegradation may be occurring. These data suggest that the former operations and disposal at the Honeywell facilities are the primary sources of PAHs to the lake system. Notably, while there is much evidence to define the likely sources of PAHs contamination, the estimates for the magnitudes of the loss terms for the lake are substantially less than the inputs. Although not estimated here, it is likely that the in-lake degradation loss mechanisms play a major role in the PAH budget for the lake.

These sources agree well with the contaminant distribution maps (Figures 5-20 through 5-22), which show elevated concentrations of LPAHs centered in front of the Honeywell shoreline and HPAHs distributed across the south end of the lake.

These results also agree well with Hubbard (1996), who indicated suspected sources of naphthalene in front of the Honeywell lakeshore area, with slightly elevated concentrations of naphthalene located south of Lakeview Point (Wastebeds 1 through 8) and north of the causeway at the Willis Avenue site, higher concentrations south of the causeway, and the highest concentrations in the southern corner of the lake adjacent to Harbor Brook (Hubbard, 1996). Hubbard also indicated a source of PAHs is located along the southern shore between Ley Creek and the entrance to the Barge Canal (Onondaga Creek), in front of the Oil City area.

6.2.5.6 Principal Components Analysis and Other Forensic Evidence

A PCA was conducted as a means to further identify Honeywell-related PAH contamination (see Appendix I). The PCA performed on the sample-normalized mass fractions of the 17 PAH compounds reported as per standard procedures eliminated sample concentration as a variable, and the PCA was able to focus on the relative proportions of the various PAHs in the samples. The full PCA results are presented in Appendix I.

The PCA produced further evidence in support of the PAH interpretation described previously. The PCA identified two basic PAH patterns based on mass fraction from the Onondaga Lake sediment data, as follows:

- PAH pattern 1: The first pattern consisted of LPAHs; specifically, naphthalene.
- PAH pattern 2: The second pattern identified those samples primarily consisting of the HPAHs.

As discussed above, the samples closest to the East Flume exhibited the highest PAH concentrations. These concentrations exhibited PAH pattern 1 (naphthalene-dominant). The samples farthest from the East Flume exhibited the lowest PAH concentrations. These concentrations exhibited PAH pattern 2 (high molecular weight dominant). These patterns again agree with the conclusion that the major source of the LPAHs is likely from the Honeywell operations. In addition, PAH pattern 1 indicates a source of PAHs that is almost entirely naphthalene. Analysis of the tar from the Semet Residue Ponds found naphthalene to be the only PAH in the waste at high concentrations (about 10 percent) (J. Hassett, pers. comm., 2002). This waste was disposed of at the Semet Residue Ponds site and in other locations, including the in-lake waste deposit and the Wastebed B/Harbor Brook site, implicating them as likely sources of the waste contaminating the lake with naphthalene.

Another comparison which complements these analyses is an examination of two additional compounds, PXE and PTE, in lake sediments (as introduced in Chapter 4). These compounds were a byproduct of benzene production using the Semet process (Hassett, 1994). Therefore, any detection of these compounds in lake sediments would be indicative of contamination by the Honeywell operations. PTE and PXE are found in the Semet Residue Ponds tars at levels higher than naphthalene (about 10 and 20 percent, respectively). These compounds have physical properties similar to PAHs and would be expected to behave in a similar fashion in the environment, and are quantitated using analytical techniques similar to those applied to PAH analysis. Hassett and Hubbard (1995) identified a source area of these compounds, coincident with naphthalene, in front of the Honeywell properties. The chromatograms of about 30 sediment samples were examined and the concentrations of PXE and PTE were quantified by TAMS. These samples were selected so as to represent several areas of the lake, including:

- The in-lake waste deposit.
- Lake sediments in front of the Semet Residue Ponds site.
- Lake sediments in front of the Willis Avenue site.
- The delta of Harbor Brook.
- The area in front of the Metro discharges.
- The sediments in front of Oil City.
- The Ninemile Creek delta.
- The deep basins of the lake.

The samples were selected such that many of the evaluated samples were obtained from the in-lake waste deposit while a single sample was obtained from each of the other locations. By averaging the in-lake deposit samples to a single result, a simple observation can be made for four of the stations; specifically, for the Semet, Willis, Harbor Brook, and in-lake waste deposit samples, the ratio of PXE+PTE to naphthalene varies only marginally, from 2 to 3, on a weight-to-weight basis. This is distinctly different from the Oil City sample, which had no detectable PXE+PTE but had naphthalene at 120 mg/kg. The samples from the Ninemile Creek and Metro areas were non-detect for both parameters and so were free of this Honeywell-related PAH contamination. These results further support the contention developed from the PCA that the major source of naphthalene and PXE/PTE in the lake was the Honeywell facilities.

6.2.6 Polychlorinated Biphenyls

The purpose of this section is to describe the distribution, sources, transport, and fate of PCBs in Onondaga Lake. PCBs are dielectric fluids mass produced from the 1940s to the mid 1970s, principally for use in electrical equipment. They were also used in many other industrial applications, wherever high-temperature stability and insulating properties were desired. They were sometimes included in paints, hydraulic fluids, "carbonless" paper, and other manufacturing. Their high degree of chlorination makes them very stable and difficult to break down, resulting in their longevity when released to the environment. There were several users of PCBs in the Onondaga lake watershed, including the Honeywell facilities and the General Motors (GM) facility on Ley Creek.

6.2.6.1 Environmental Persistence and Fate

With the higher solubility and lower K_{ow} values, low molecular weight PCBs (LPCBs), can remain largely in the water column and further escape from water via volatilization. High molecular weight PCBs (HPCBs) have a greater tendency to bind to solids as a result of strong hydrophobic interaction. The PCBs currently in Onondaga Lake sediments are expected to remain sorbed to natural organic carbon in the sediments where they tend to persist with half-lives on the order of months to years. PCB congeners with three or less chlorine substitutes (major components in Aroclors 1221 and 1232) are considered to be non-persistent, while those with five or more chlorines (major components in Aroclors 1248, 1254, and 1260) are not readily degraded and are considered to be persistent. As noted in Chapter 5, PCB contamination in the lake sediment is dominant with heavy Aroclors, such as 1248, 1254 and 1260. Therefore, PCBs in Onondaga Lake sediments are expected to persist for many years.

6.2.6.2 Inputs to Onondaga Lake

Tributary Loads

Surface water concentrations of PCBs were measured by Honeywell/Exponent at Ninemile Creek and Geddes Brook in 1998. A total of 24 samples were collected at four different stations, and none of them had detected PCBs. These data suggest that Ninemile Creek may not contribute a significant amount of PCBs to the lake.

Sediment concentrations were used to estimate the loading using the procedures described in Section 6.2.1. As shown in Table 6-46, the highest loads were estimated for Ley Creek, with 23 kg/yr of Aroclor 1016, 3.8 kg/yr of Aroclor 1242, and 1.1 kg/yr of Aroclor 1260. Load estimates were also high for Onondaga Creek, with 22 kg/yr of Aroclor 1260. In Onondaga Creek, loadings of other Aroclors were not greater than about 500 g/yr. Aroclor input from Tributary 5A, Ninemile Creek, Harbor Brook, and Bloody Brook ranged from 15 to 770 g/yr. Aroclor loadings from the East Flume and Sawmill Creek are relatively small, less than 10 g/yr. This suggests that the contribution of PCBs to the lake from Ley Creek is the most significant among all the tributaries.

Previous investigations using PISCES passive sampling devices (a semiqualitative method) did not detect PCBs at significant levels in Harbor Brook or Ninemile Creek (Hubbard, 1996). The concentrations of PCBs in Onondaga Creek are typically lower than in the Barge Canal and, therefore, are not an important source to the canal or lake. But one exposure period was found to show higher PCBs in Onondaga Creek, with Aroclor 1260 predominant, which indicates that Onondaga Creek may at times be a significant source to the canal and lake. PCBs were detected consistently in Ley Creek at levels greater than those found in the lake, indicating that Ley Creek could be a significant source of PCBs to the lake. Therefore, the findings of this RI are consistent with the results of this previous investigation.

Groundwater Advection

Groundwater data collected in 1997, 1999, and 2001 from wells along the lakeshore were used to estimate the groundwater advection load to Onondaga Lake in front of the Willis Avenue, Semet Residue Ponds, and Wastebed B/Harbor Brook sites. Details of the calculations and model used can be found in Sections 6.2.1 and 6.1.1.3.

Only one groundwater sample was detected with Aroclor 1260. All others were not detected with a detection limit of $0.5 \mu g/L$. Using half the detection limit, the estimated load of each Aroclor is the same (approximately 0.25 kg/yr). Therefore, the load of total PCBs is about 2 kg/yr, using the sum of all Aroclors as total PCBs.

Flux from Sediment Porewater

The sediment porewater flux for PCBs was developed in a similar manner as for the other organic CPOIs. Due to lack of porewater measurements, the 0 to 2 cm surface sediment concentrations were used to calculate the loads of PCBs to Onondaga Lake via porewater diffusion, as discussed in Section 6.2.1. This assumes the system is in equilibrium.

Loads via porewater diffusion/advection were calculated separately, based on LPCB and HPCB concentrations in the sediment. From these estimations, it appears that porewater diffusion is an important mechanism for LPCB input to the water column. LPCBs input to the water column via diffusion is on the order of 1.4 kg/yr, while the HPCBs porewater diffusion input is much less (9 g/yr). Porewater advection

contributes less to PCB input to the water column. The load of LPCBs via porewater advection was estimated to be 210 g/yr and only 2 g/yr for HPCBs (Table 6-47).

Precipitation

The input of PCBs to Onondaga Lake via precipitation to the lake surface was estimated from rainfall rates, as discussed in Section 6.2.1.

Concentration of PCBs in precipitation was not determined for Onondaga Lake. Average total PCB concentrations in precipitation were reported to be 13 ng/L at Camden, NJ, an urban-industrial site near Philadelphia, PA, and 3.9 ng/L at Jersey City, NJ, an urban-industrial site near New York City (Van Ry et al., 2002). Seasonal snow cores were collected in northern and central Minnesota and at Eagle Harbor, Michigan on Lake Superior between 1982 and 1992, where snowpack concentrations of total PCBs ranged from 1 to 14 ng/L (Franz and Eisenreich, 2000). Considering the similar site characteristics, the average PCB concentration in precipitation to Onondaga Lake was assumed to be in the same order of the data reported above. Thus, 10 ng/L was used in the calculation. This concentration gives an estimate of 130 g/yr of PCB input to the lake surface from precipitation.

In-Lake Resuspension

The resuspension model described in Section 6.1.3 is used to estimate the load of PCBs from sediment to water column via resuspension during the stratification period. Due to the lack of porewater data, the 0 to 2 cm surface sediment concentrations were averaged and applied to the model. Since the samples were distributed unevenly and many samples with the highest concentrations were located within small areas, both area-weighted average concentrations and simple average concentrations were used in the calculation. Over the stratification period, the resuspension loading for LPCBs was about 1.7 to 2.4 kg. The estimated load of HPCBs was relatively small at about 0.4 kg (Table 6-47).

6.2.6.3 Losses from Onondaga Lake

Volatilization

In the 1992 sampling event, PCB concentrations were measured in water samples collected at depths of 6 and 12 m. All samples were non-detected, with a detection limit of 1 μ g/L (the detection limit for Aroclor 1221 was 2 μ g/L). However, in another study (Hubbard, 1996), PISCES samples were collected mainly in the southern basin of the lake and the dissolved PCB concentration was estimated to be around 0.01 to 0.03 μ g/L. On this basis, 0.03 μ g/L was used as the dissolved-phase PCB concentration to provide an upper-bound estimate of loss of PCBs due to volatilization.

Molecular diffusivity in air and the Henry's Law constant were assumed to be 0.0527 cm²/sec and 0.00025 atm/mol-m³, respectively, for PCBs based on the study performed in the Hudson River (TAMS/USEPA, 2002). As indicated by 1992 and 2000 sediment data (see Chapter 5), PCB contamination in Onondaga Lake mainly consists of Aroclor 1242, Aroclor 1248, Aroclor 1254, and Aroclor 1260. The average

molecular weights of these four Aroclors was applied to estimate the molecular diffusivity in water using the equation given in Section 6.1.1.4.

To be conservative, a zero concentration was assumed for the air above the lake. The loss of PCBs via volatilization is 23.5 kg for the nine-month period when ice is not covering the lake. It is noted that the K_{OL} value calculated in this study is lower than the number in Hudson River study (TAMS/USEPA, 2000), reflecting the lower wind speeds and lotic conditions of Onondaga Lake.

Outflow

Assuming that volume of the lake is constant, the outflow from the lake will be equal to the inflow from tributaries and Metro. The sum of tributary flow is about 530×10^6 m³ per year. Based on Hubbard (1995), it was found that the dissolved-phase total PCB concentrations adjacent to Ninemile Creek were about 2.5 to 10 ng/L, which are lower than the concentrations typically found in the southern basin. As shown in Chapter 5, Figure 5-23, the PCB contamination level for the surface sediment (0 to 2 and 0 to 30 cm) in the Ninemile Creek delta is similar to that for the northern basin. Therefore, 2.5 to 10 ng/L is assumed to be the dissolved-phase concentration in the lake discharge. Data from Lake Michigan indicate that dissolved PCBs accounted for 75 percent of the total PCBs measured in all water samples (Offenberg et al., 2000). Therefore, the whole-water PCB concentration in the discharge is about 3 to 13 ng/L, which results in a discharge load of approximately 1.6 to 7 kg/yr.

Particle Settling

In water, adsorption to sediments and organic matter is a major fate process for PCBs, especially for highly chlorinated congeners that have relatively high K_{∞} values. Therefore, sedimentation is considered to be one of the major loss processes from the water column. Littoral zone surface sediment concentrations were applied to estimate the settling rate of PCBs to the lake bottom. With the higher concentration in the sediment, LPCBs have the higher sedimentation load (on the order of 1.6 kg over the stratification period), while the sedimentation load of HPCB is about 1 kg (Table 6-48).

6.2.6.4 In-Lake Processes

PCBs can leave the water column by partitioning onto sediments and suspended particulates, and by volatilization at the air-water interface. They can also be immobilized for relatively long periods of time in aquatic sediments. The adsorption of dissolved PCBs onto solids (suspended particulates and sediments) is greatest for solids composed primarily of organic matter and clay. The more highly chlorinated PCBs, which have lower water solubilities and higher octanol-water partition coefficients (K_{ow}), have a greater tendency to bind to solids as a result of strong hydrophobic interactions. In contrast, the LPCBs, which have higher water solubilities and lower partition coefficients, sorb to a lesser extent to solids and remain largely in the water column. Volatilization of highly chlorinated PCBs in the water column is reduced significantly by the sequestration of solids compared to the lightly chlorinated PCBs, in which volatilization may be only slightly affected.

In addition to volatilization and sorption onto sediments, PCBs can leave the water column by concentrating in biota directly from water. The BCFs of PCBs in aquatic organisms are directly proportional to partition coefficients and lipid contents of the organism, and are congener-specific. BCFs in various fresh water and marine species are generally in the range of 5×10^2 to 4×10^4 for lower chlorinated PCB congeners and about 1×10^3 to 3×10^5 for tetra- to hexa-PCBs (congener numbers BZ 70, 101, 110, and 136). The BCFs for the higher chlorinated homologs drop off after a certain point because these larger molecules do not readily pass through biological membranes.

Bioaccumulation factors (BAFs) of PCBs increase with higher chlorination and lower water solubility. Less chlorinated PCBs (1 to 4 chlorines) are readily taken up by organisms, but are also readily eliminated and metabolized. Thus, these homologs are not bioaccumulated to a great extent. The most highly chlorinated congeners (7 to 10 chlorines) occur in low concentrations in the environment, and are tightly bound with soil, sediment, and organic matter. Thus, these PCBs are also not significantly bioaccumulated. These PCBs, which have log K_{ow} values greater than 5, appear to enter biota through food-web transfer from sediment, which is less efficient. On the other hand, the penta-, hexa-, and hepta-PCBs are all bioavailable and resistant to degradation in organisms; and these PCB homologs bioaccumulate in organisms to the greatest extent.

In water, abiotic transformation processes such as hydrolysis and oxidation do not significantly degrade PCBs. Photolysis appears to be the only significant abiotic degradation process in water. The estimated photolysis half-lives of mono- through tetrachlorobiphenyls, with summer sunlight at a shallow water depth (less than 0.5 m), range from 17 to 210 days.

The rate of PCB biodegradation in water is dependent on both individual congener structure and environmental conditions. Biodegradation in surface waters is primarily an aerobic process. The less chlorinated mono- and dichlorobiphenyl congeners are more likely to dissolve in water than the more chlorinated congeners. These congeners are also more likely to biodegrade under aerobic conditions. Biodegradation is potentially a more important process in sediment than in water, particularly for the more highly chlorinated congeners, for at least three reasons: the higher numbers of microorganisms present, the opportunity for anaerobic biodegradation, and the preferential partitioning of PCBs to sediment.

PCBs, particularly the highly chlorinated congeners, adsorb strongly to sediment, where they tend to persist with half-lives on the order of months to years. Biodegradation has been shown to occur under both aerobic and anaerobic conditions and is a major degradation process for PCBs in sediment. Aerobic biodegradation of PCBs in the environment occurs mainly in surficial sediments. PCB congeners with three or less chlorine substituents (major components in Aroclors 1221 and 1232) are considered to be non-persistent, while those with five or more chlorines (major components in Aroclors 1248, 1254, and 1260) are not readily degraded and are considered to be persistent. Tetrachlorobiphenyls (major components in Aroclors 1016 and 1242) are intermediate in persistence.

PCBs are slowly biodegraded in anaerobic environments by reductive dechlorination, resulting in the formation of less-toxic mono- and dichlorobiphenyl congeners, which are aerobically biodegradable. The

rate, extent, and specificity of anaerobic dechlorination can vary greatly, even in the same sediment, based on a number of environmental factors, including:

- Previous exposure to PCBs or PCB-like compounds.
- Electron acceptor availability.
- Bioavailability.
- Presence of co-contaminants.
- Oxygen tension.
- Redox level.
- Temperature.
- pH.
- Salinity.
- Inhibitory compounds.
- Available carbon and nutrients.
- Trace metals.

Optimum rates of PCB dechlorination usually occur in the concentration range of 100 to 1,000 ppm (wet weight). Below a certain threshold concentration (less than 50 ppm), the rate of dechlorination is often very slow or non-quantifiable. It has also been shown that the higher chlorinated congeners in PCBs are susceptible to reductive dechlorination in sediment. Although biodegradation of higher chlorinated congeners may occur very slowly in the environment, no other degradation mechanism has been shown to be important in environmental aquatic systems; therefore, biodegradation may be the ultimate degradation process in natural water.

6.2.6.5 In-Lake Distribution and Likely Sources

PCBs are widely distributed in Onondaga Lake, with large areas of the southern deep basin showing significant contamination. Maximum concentrations occurred in the southern basin littoral zone. Elevated levels of PCBs were also observed in the southeastern corner of the lake near Ley Creek. The Aroclor pattern found along the causeway near the Honeywell Willis Avenue site was identified as primarily 1248 and 1254, which is a much heavier mixture than that found elsewhere in the lake. Aroclor 1248 is also a significant fraction of the total PCB mixture in front of Harbor Brook. This pattern is different from that found in the rest of the lake and indicates that a distinct source exists here, possibly Honeywell operations.

Based on the presence of PCBs in their sediments, the tributaries appear to be the major ongoing sources to the lake. In particular, Onondaga Creek (Aroclor 1260) and Ley Creek (Aroclors 1221, 1242, and 1260) are the most significant of the tributaries, based on loads derived from sediment data. PCBs are also released from the in-lake waste deposit via resuspension, but this appears to be a much smaller flux than that delivered by the tributaries. Losses of PCBs from the lake occur primarily by volatilization for the LPCBs and by particle settling for the HPCBs. Within the sediments, biodegradation is likely but has not been reported to date. Biological exposure is an amalgam of loads and existing PCB inventory, since there

are several exposure pathways. Thus, it is unclear whether historical or recently discharged PCBs are responsible for increased biota levels.

6.2.7 PCDD/PCDFs

This section describes the distribution, sources, transport, and fate of PCDD/PCDFs in Onondaga Lake. PCDD/PCDFs are highly toxic compounds that are frequently produced during chemical manufacturing. More recently, they have been produced and discharged to the environment as a result of combustion processes, and in particular by incinerators and other sources of incomplete combustion. Based on evidence collected by Honeywell from their sites, PCDD/PCDFs were apparently produced as the result of a fire in the former chlorination buildings in the 1930s and as trace contaminants during the various manufacturing operations. Several patterns of PCDD/PCDFs exist in the lake, some of which may be traced to Honeywell.

PCDD/PCDF data for the site are limited to sediment and soil samples. Sediment samples in the littoral zone of the lake were selected for PCDD/PCDF analysis from the Ninemile Creek delta through the south end of the lake to Ley Creek. Sediment samples also were taken from several tributaries. Because surface water and groundwater concentrations were not measured, conservative estimates of these values will be made whenever possible. These estimates give an indication of the magnitude of the PCDD/PCDF fluxes that are dependent on surface water and groundwater concentrations.

6.2.7.1 Environmental Persistence and Fate

PCDD/PCDFs have very low solubility and low volatility. PCDD/PCDFs in Onondaga Lake sediments will tend to remain sorbed to the organic moieties of sediment, and future inputs will generally sorb to particulates and be deposited on the lake bottom. Although dioxin and furan congeners undergo varying degrees of dechlorination under anaerobic conditions, the half-lives of these compounds are greater than ten years in most sediment environments and their persistence is classified as high. These compounds are likely to accumulate in sediments or aquatic organisms and will generally persist for several decades.

6.2.7.2 Inputs to Onondaga Lake

Tributary Loads

The surface water carried into the lake by the tributaries is a potential source of PCDD/PCDF contamination to the lake. PCDD/PCDF concentrations in sediments were used to estimate tributary loads.

Sediment concentrations were measured in the lower East Flume and lower Ninemile Creek. 870 mg are estimated to enter the lake annually from the lower East Flume, and 4,100 mg are estimated to enter the lake annually from lower Ninemile Creek (see Table 6-49). This is somewhat counterintuitive, because the sediments near the East Flume are much more contaminated than the sediments near Ninemile Creek (see Chapter 5, Figures 5-26 and 5-27). These findings illustrate the fact that the lake bottom in front of the East

Flume is actually waste material from Honeywell, and has contamination concentrations out of proportion to any ongoing sources in the area, but also reflects the much greater flow through Ninemile Creek, which compensates for the difference in concentration. Nonetheless, the result may indicate that the load calculated for Ninemile Creek is an overestimate. About 7,600 mg per year total PCDD/PCDFs are estimated for Ley Creek using sediment concentrations in the vicinity of the General Motors – former Inland Fisher Guide (GM – IFG) facility. Since these Ley Creek sediment data were collected between 3 and 6.5 km upstream from Onondaga Lake, the loading estimate is considered uncertain and may be an upper-bound estimate. No estimate of loads from the remaining tributaries can be made.

Groundwater Advection

An estimate of the contribution of PCDD/PCDFs from the groundwater to the lake could not be made. Typically, PCDD/PCDFs will strongly adhere to organic matter in soils. Being highly hydrophobic compounds with low aqueous solubility, PCDD/PCDFs are unlikely to leach into the groundwater. Most of the PCDD/PCDFs entering the groundwater would be associated with particulate matter (ATSDR, 1998b). Given the chemical and physical properties of PCDD/PCDFs, groundwater loads to the lake are likely insignificant.

Flux from Sediment Porewater

The diffusion and advection of porewater has the potential to create large contaminant fluxes to the lake. The magnitude of the flux for PCDD/PCDFs was estimated as described in Section 6.2.1. An estimate of the concentrations in porewater was made using the 0 to 15 cm sediment concentrations. It is expected that the contribution of PCDD/PCDFs to the lake from porewater would be small, because of the nature of PCDD/PCDFs (hydrophobic, low solubility).

As expected, the yearly contribution for PCDD/PCDFs from porewater is low, with 12 mg/yr entering the lake through advection and 7 mg/yr through diffusion (Table 6-49). This amount is two orders-of-magnitude less than that from the other input mechanisms. Approximately 75 percent of this contaminant load is from tetrachlorodibenzofuran (TCDF), due to the high concentrations of TCDF in lake sediments near the East Flume and Harbor Brook and its relatively low K_{∞} value. Pentachlorodibenzofurans (PeCDFs) contribute approximately 20 percent of the load, largely due to the relatively low K_{∞} value for this contaminant. PeCDFs have the highest homolog concentration in fish sampled from Ninemile Creek and the East Flume area. Octachlorodibenzodioxin (OCDD) concentrations have the highest homolog concentration in some of the surface samples, but because of their high K_{∞} value, their contribution to the porewater is low, ranging from 1×10^{-5} mg/yr near the East Flume to 5×10^{-3} mg/yr near Ninemile Creek.

Precipitation

PCDD/PCDFs have been distributed over large areas by atmospheric transport. This contamination is largely attributable to combustion processes. While in the air, the contaminants partition between the vapor and particle-bound phases, with most of the contaminants in the particle-bound phase. This process is

controlled by atmospheric temperature and the vapor pressure of each contaminant. PCDD/PCDFs are effectively removed from the atmosphere by precipitation (wet deposition) and particle dry deposition (ATSDR, 1998b).

Direct measurements of wet and dry deposition concentrations of PCDD/PCDFs were not available. To estimate these values, the results of a study of the deposition of PCDD/PCDFs in Indianapolis were used (Koester and Hites, 1992). It is reasonable to apply the results of the Indianapolis study to the Syracuse area, because the average homolog pattern was typical of an urban region having dry deposition fluxes with considerable amounts of homologs other than OCDD. Wet deposition for Onondaga Lake was calculated by multiplying the average estimates of the rain concentrations by the volume of rain that fell on Onondaga Lake in 1992. Dry deposition was calculated by multiplying the average fluxes by the area of Onondaga Lake. The sum of the wet and dry deposition contributions is presented in Table 6-49.

Atmospheric deposition potentially provides a significant quantity of PCDD/PCDFs to the lake. Using the Indianapolis study results, about 3.7 g/yr would be deposited on Onondaga Lake. About 45 percent of this amount would be from OCDD and 20 percent would be from hexachlorodibenzodioxin (HxCDD). This process produces the second largest calculated input of PCDD/PCDFs to the lake, behind the tributary loadings.

In-Lake Resuspension

Resuspension of PCDD/PCDFs bound to sediment particles increases the transport of the compounds in the aquatic environment. An estimate of the amount of resuspension is presented in Table 6-49. For all homologs, the amount of resuspension is approximately 2 g for the stratified period, with OCDD making up nearly half of this amount. HxCDD has the next highest amount resuspended, at 0.4 g for the stratification period, and TCDF has the third highest amount resuspended, at 0.2 g.

6.2.7.3 Losses from Onondaga Lake

Volatilization

Volatilization is a process that can remove PCDD/PCDFs from the water column to a minor extent. Because the Henry's Law constants for these compounds are $low(1.31 \times 10^{-6} to 146 \times 10^{-6} atm-m^3/mol)$, removal by this process is likely to be slow, controlled by gas-phase resistance. In general, volatilization is an insignificant process of loss compared to adsorption to particles and sedimentation. An estimate of the amount volatilized per year was calculated using average sediment concentrations and the partition coefficients for the contaminants, as described in Section 6.2.1. The amount volatized per year for all homologs is estimated to be 5 g. Of the total load, 89 percent is from TCDF and 4 percent is from PeCDF.

Outflow

The amount of CPOIs exiting Onondaga Lake through the outlet was calculated by summing the volume of water entering the lake each day during the study period and multiplying that value by the average surface water concentration of the CPOIs. Because surface water concentrations of PCDD/PCDFs were not measured in Onondaga Lake, a surface water concentration was estimated from the average sediment concentration at the nearest location, as discussed in Section 6.2.1. The outlet is closest to the Ninemile Creek delta. These sediments were lower in concentration than the southern basin samples and provide a rough estimate of conditions near the outlet. As shown in Table 6-49, the estimated discharge for all homologs is 4 g/yr. This low loss term is the same order-of-magnitude as volatilization. Of the total load, 63 percent is from TCDF, 12 percent is from PeCDF, and 12 percent is from OCDF.

Particle Settling

Resuspended particles in the littoral zone may drift to the center basins and gradually fall into the profundal zone. This process of particle settling focuses the contamination into the deep basins. The amount of each contaminant carried into the profundal zone each year was calculated and is presented in Table 6-49. Note that the core from near Ley Creek was not used to estimate the PCDD/PCDF concentration on particles from most of the littoral zone as was done for other CPOIs, because this core was located near a source and had a correspondingly high concentration.

Assuming that the northern areas of the littoral zone (no measurements of these areas are available) are less contaminated, the average concentration of the samples collected near Ninemile Creek was used to represent the area between Tributary 5A and Ley Creek. The reach between Ley Creek and Onondaga Creek was separated out and represented by the core taken near Ley Creek. The estimate of particle settling is relatively large, totaling 21 g for all homologs for the stratification period. The largest contributions to this total are OCDD (10 g), heptachlorodibenzodioxin (HpCDD) (4 g), and TCDD (2 g).

6.2.7.4 In-Lake Processes

PCDD/PCDFs are removed from the water column to a minor extent by volatilization to the atmosphere, with binding to particulates and sediment or bioaccumulation by aquatic biota being more significant processes.

PCDD/PCDFs have Henry's Law constants ranging from 1.31×10^{-6} to 146×10^{-6} atm-m³/mol. These values indicate that volatilization from water is likely to be slow. The more-chlorinated homolog classes (TCDD, PeCDD, HxCDD, HpCDD, and OCDD) have lower Henry's Law constants than the less-chlorinated homolog classes (monoCDD, diCDD, and triCDD). Thus, volatilization from the water column is not expected to be a very significant loss process for the TCDD through OCDD congeners as compared to adsorption to particulates.

In general, the Henry's Law constants decrease with increasing chlorine number as a result of the decrease in vapor pressure and water solubility. Volatilization half-lives for 2,3,7,8-TCDD were calculated in another study for ponds and lakes (32 days) and for rivers (16 days) (ATSDR, 1998b). However, when the effects of adsorption to sediment are considered, the volatilization model predicts an overall volatilization removal half-life of over 50 years.

Due to low vapor pressure, low aqueous solubility, and high hydrophobicity, PCDD/PCDFs strongly adsorb to sediment particles. Therefore, the primary removal mechanism for PCDD/PCDFs from the water column is sedimentation, with 70 to 80 percent of the PCDD/PCDFs being associated with the particulate phase. Aquatic sediments may be an important, and ultimate, environmental sink for all global releases of PCDD/PCDFs. PCDD/PCDFs bound to sediment particles may be resuspended in the water column if the sediments are disturbed. This could increase both the transport and availability of the PCDD/PCDFs for uptake by aquatic biota, as is reflected in the Honeywell/Exponent 2000 fish data and NYSDEC 1999 fish data. In 2000, fish were collected from two areas: in front of the Honeywell facilities and in front of Ninemile Creek. The two species which tend to have contact with the bottom sediments (carp and catfish) collected from in front of the Honeywell shoreline area near Harbor Brook and Tributary 5A had significantly higher concentrations of PCDD/PCDFs than the carp and catfish from in front of Ninemile Creek. PCDD/PCDF concentrations were also higher in carp and catfish than the other species obtained from both locations.

Adsorption is an important process affecting transport of hydrophobic compounds such as PCDD/PCDFs. The organic carbon fraction of the sediment is believed to be the most important factor governing the degree of adsorption of hydrophobic organic contaminants. PCDD/PCDFs adsorb more strongly to soils with a higher organic carbon content than to soils with low organic carbon content. Because of their very low water solubilities and vapor pressures, PCDD/PCDFs found below the surface sediment (top few mm) are strongly adsorbed and show little vertical migration, particularly in sediment with high organic carbon content.

PCDD/PCDFs have K_{ow} values ranging from 10⁴ to 10¹² for monoCDD through OCDD, with K_{ow} values increasing relative to increasing chlorination. Because of these physicochemical properties, PCDD/PCDFs are expected to adsorb to bedded and suspended sediments and to bioaccumulate in aquatic organisms. The bioconcentration of PCDD/PCDFs tends to increase with the degree of chlorination up to TCDDs, and then decrease as chlorination continues to increase up to the OCDD congener. The more highly chlorinated congeners, such as OCDD, appear to have the lowest bioconcentration potential, either because they are less bioavailable or because of their rapid adsorption to sediment particles, or because their large molecule size may interfere with transport across biological membranes. Because only a minute fraction of PCDD/PCDFs are dissolved in the natural environment, bioconcentration is not the primary route of exposure for most aquatic organisms.

Photolysis is a relatively slow process in water. In general, however, lower-chlorinated PCDD/PCDFs are degraded faster than higher-chlorinated congeners. Chlorine atoms in the lateral positions (e.g., 2, 3, 7, 8) are also more susceptible to photolysis than are chlorine atoms in the para-positions (e.g., 1, 4, 6, 9).

Photolysis half-lives for dissolved 2,3,7,8-TCDD in sunlight range from 118 hours in winter, to 51 hours in fall, to 27 hours in spring, to 21 hours in summer.

Various biological screening studies have demonstrated that TCDD is generally resistant to biodegradation. The half-life of TCDD in lakes has been estimated to be in excess of 1.5 yr (ATSDR, 1998b).

PCDD/PCDFs appear to be stored in the sediments of Onondaga Lake, with the highest concentrations found between Tributary 5A and Harbor Brook and near Ley Creek. Resuspension and particle settling will likely distribute the contaminated sediments in the lake to some extent, serving to focus the contamination in the profundal zone over time. PCDD/PCDFs are not likely to be removed from the actual sediment particles by processes such as porewater advection, because of their extremely high affinity for the particles.

6.2.7.5 In-Lake Distribution and Likely Sources

Sediment cores were analyzed for PCDD/PCDFs near Ninemile Creek and in the south end of the lake between Tributary 5A and Ley Creek. As shown in Chapter 5, Figures 5-26 and 5-27, the Ninemile Creek delta and the area near the Metro outlet have lower concentrations than the other measured locations. At Ley Creek and between Tributary 5A and Harbor Brook, the concentrations are higher and generally have higher concentrations at depth. Each sediment core exceeds NYSDEC wildlife bioaccumulation criteria at one or more depths, with the exception of the core taken near the Metro outfall.

A PCA of the PCDD/PCDF data was performed in an attempt to identify the source material. This analysis is presented in Appendix I. The PCA was successful in identifying three distinct types of contamination: TCDF, OCDD high mass, and OCDD low mass. Sources for each type of contamination were identified using soil and sediment samples from the surrounding sites. The spatial distribution and the deposition history for these types of contamination are consistent with the relative years of operation for each of the identified potential sources. The three contamination types may be summarized as follows:

- The predominantly TCDF contamination in the lake is similar to the soil samples collected from the Willis Chlorobenzene site and sediment samples from the East Flume. This type of contamination appears to radiate from the East Flume delta, further indicating that the Willis Chlorobenzene site soils and East Flume sediments were the sources of this contamination. A fire at the former chlorination building in the 1930s was likely a major source of PCDD/PCDFs. The chlor-alkali process and the production of chlorinated benzenes are known to generate PCDD/PCDFs as a byproduct (ATSDR, 1998b).
- OCDD high mass contamination seems to come from two sources: 1) Geddes Brook and Ninemile Creek sediments, downstream from the LCP Bridge Street site, and 2) the sediments of Ley Creek in the vicinity of the GM-IFG facility. Although no samples collected at the LCP Bridge Street site were measured for

PCDD/PCDFs, the sediments and soils from Ninemile Creek and Geddes Brook have been affected by this site and show the OCDD high mass pattern of contamination. Cores from the Ninemile Creek delta and the I-690 storm drain outfall also have this pattern, although the cores from the I-690 storm drain outfall also have TCDFs from the nearby Willis Avenue Chlorobenzene site.

Because the pattern of contamination in the core collected near Ley Creek was indistinguishable from the pattern of contamination seen at the Ninemile Creek delta and the I-690 storm drain outfall (Station S336), the source of the contamination can only be inferred, based on the spatial distribution of the contaminant patterns in the lake. There is OCDD high mass throughout the studied portion of the lake with the exception of the East Flume-related contamination. The East Flume area seems to be a divide in the lake between the OCDD high mass contamination likely emanating from Ninemile Creek and from the contaminated sediments of Ley Creek.

The OCDD low mass contamination appears to be deposition from the atmosphere. Atmospheric deposition samples typically are high in OCDD contamination relative to the other homologs. The concentrations in the sediment characterized as OCDD low mass were 1 to 10 ng/kg, much lower than the other samples. Core segments with OCDD low mass were located in the deepest portions of the core, below site-associated contamination.

In summary, ongoing discharges to the lake via the East Flume, Ninemile Creek, and potentially Ley Creek continue to deliver substantial amounts of PCDD/PCDFs to the lake. As estimated in this RI, these represent the largest contribution to the lake. The nature of these discharges suggests that the Ninemile Creek source and the potential Ley Creek source are OCDD-dominant, while the East Flume pattern is TCDF-dominant.

Once in the lake, PCDD/PCDFs tend to remain on the sediments, where they are available for biological uptake. There is little loss via volatilization or degradation processes. Historically, it appears that both OCDD-dominant and TCDF-dominant discharges have occurred, originating from the Honeywell facilities, and potentially from the GM-IFG facility. Of these, the TCDF-dominant releases in the East Flume/Willis Avenue site area would be of greater concern environmentally because of their high degree of toxicity.

6.3 Calcite and Calcite Components

The precipitation and deposition of calcium carbonate, usually as calcite, is a widely observed phenomenon in oversaturated hard-water lakes. According to Effler et al. (1996c), from 1980 to 1990, both the epilimnion and hypolimnion waters of Onondaga Lake were oversaturated with respect to the solubility of calcite, with the degree of oversaturation greater in the epilimnion. The precipitation of calcite has broader importance than its effects on deposition rates, including the likely influence of the cycling of phosphorus, dissolved organic carbon (DOC), and other particles that serve as nuclei for precipitation, and it may also decrease water clarity (Effler et al., 1996c).

As part of the investigation of the ionic waste contamination in Onondaga Lake, Honeywell and its consultants constructed a model of carbonate and calcium behavior based on relatively well known relationships of carbonate equilibria that was reevaluated by NYSDEC (NYSDEC/TAMS, 1998a). The model was to provide a framework for understanding the current and historical conditions relating to calcite precipitation within Onondaga Lake and to represent both internal and external loads of alkalinity, total inorganic carbon, and calcium to the lake. The model was then intended to serve as a tool for the assessment of potential remedial activities and their subsequent effects on lake conditions. However, Honeywell's model modeling report was disapproved by NYSDEC because the data used to calibrate the model were not critically reviewed and were not appropriate for model calibration.

The NYSDEC revision of the calcite modeling report (NYSDEC/TAMS, 1998a) reviewed the water chemistry data used in the steady-state model of calcite precipitation developed by Honeywell/PTI/HydroQual, and presented an alternative method of evaluating the effects of Honeywell discharges on calcite deposition. The report concluded that Honeywell's calculations of calcite precipitation were flawed because most of the total inorganic carbon (TIC) data used in the model were inaccurate, and that the alkalinity and TIC balances developed in the model were incorrect. The revised report states that other data are more internally consistent and appropriate for use in the steady-state model. Although the data presented in the NYSDEC report appeared to be more consistent, they were not used in a predictive model. Rather, two non-modeling alternative approaches to evaluating the historical patterns in calcite deposition were used. These approaches use data from sediment cores that were sufficiently deep to span both the opening and closure of the Honeywell facilities and sediment traps that span the period of closure of Honeywell facilities.

In the first approach, the vertical pattern of calcite concentration in sediment cores was determined and related to historical events in order to estimate the influence of Solvay waste discharges from the soda ash facility on calcite deposition rates. The age of sediments at various depths was determined using event markers such as pollen, diatoms, metal concentration, and radionuclides. The calcite concentrations can be converted into accumulated masses over periods of time that are bracketed by the event markers using water contents or bulk density and solids density of the sediment. This yields relative average fluxes for the time interval represented by the sediment layers. Sediment cores collected by Rowell in 1988 (Rowell, 1992) and Honeywell/PTI in 1992 (PTI, 1993d) were used for the analysis.

To calculate the flux of calcite, a solids fraction of 0.7 and a bulk density of 1.5 g/cm^3 were assumed for all sediment intervals. Using calcium carbonate concentrations from the core at Station S51 in the southern basin, along with an assumed solids content of 0.7, it was estimated in the revised report that the flux of calcite to the coring site increased from 3,100 mg/m²-day prior to 1884 (when the Solvay Process Company [predecessor of Honeywell] began operation) to 8,800 mg/m²-day during operation of the plant. Similarly, it was estimated using data from Rowell (1992) that the flux increased from 2,300 mg/m²-day

to 7,900 mg/m²-day.⁴ It was concluded that calcite deposition to sediment increased by a factor of 2.8 to 4 following commencement of operations at of the Solvay Process Company.

If the calculation of calcium carbonate flux is repeated using water contents that were measured in core S51 (range 0.14 to 0.43 g solid/cm³, average 0.31 g solid/cm³) rather than assuming a solids content of 0.7, the estimated average calcium carbonate flux for the 100 years prior to Solvay Process Company (1786 and 1884) is approximately 1,800 mg/m²-day. For the period of 1884 to 1992, the estimated flux is approximately 3,900 mg/m²-day. This time period includes the 102 years of soda-ash industry discharges and six years of post-closure conditions. Including the six years of post-closure conditions has a minor effect (<5 percent) on the calculated flux for the period during which the soda-ash industry was operating, so it is assumed that the calculated flux is representative of conditions during operation. These values are lower, and suggest that the calcium carbonate flux increased during operation of the soda ash facility by a factor of about 2.2.

In a separate approach to estimating the effect of Honeywell processes on calcium carbonate deposition, fluxes were measured with sediment traps for several years preceding (1980, 1981, and 1985) and following closure of the Honeywell facility in 1986 (1986 through 1991) (Womble et al., 1996). Note that the estimates for deposition after closure of the Honeywell Main Plant still include the ionic loadings from the wastebeds, and, therefore, do not represent a return to pre-Honeywell conditions.

Prior to closure, fluxes in traps ranged from $\leq 10,000 \text{ mg/m}^2\text{-}day$ to about 40,000 mg/m²-day, and averaged 19,600 mg/m²-day. Following closure, fluxes in traps ranged from $\leq 500 \text{ mg/m}^2\text{-}day$ to about 20,000 mg/m²-day, and averaged 8,200 mg/m²-day. Because the traps were deployed only during the summer when calcium carbonate precipitation is greatest, these average fluxes are not annual averages. Annual average fluxes were approximated by assuming no deposition in the winter and half the summertime flux in the spring and fall (Womble et al., 1996). The approximated annual average fluxes before and after closure were 13,000 and 5,500 mg/m²-day, respectively. These estimates suggest that calcium carbonate deposition decreased by 60 percent following closure of the Honeywell facility. Applying this decrease as a minimum estimate of the original increase in calcite precipitation (from 5,500 to 13,000 mg/m²-day) suggests that the Honeywell discharges increased the calcite precipitation by a factor of 2.5.

These estimates vary in the absolute flux rates measured, which is not unexpected, as these types of measurements tend to be very location-specific, reflecting local deposition rates. However, the estimates all generally agree that the rate of calcite deposition increased by at least a factor of two while the Honeywell Solvay process was in operation.

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⁴Note that these fluxes are estimated at the coring site and do not necessarily represent the flux to the lake as a whole. These flux estimates are most useful as relative measures; i.e., for evaluating changes in the flux at the coring location over time. These relative changes can be used to infer parallel relative changes in the actual sources to the lake. For example, a 50 percent decline in the calcite flux at a specific coring location can generally be inferred to represent a 50 percent decline in the lake.

Calcite precipitation has greatly declined since the cessation of ionic discharges (Womble et al., 1996). This decline has served to substantively change the lake's chemistry and alter the overall deposition rate to the sediments. As discussed in Section 6.1.4, this is likely to be the reason for the rise in many metal concentrations in the sediments seen in the late 1980s in recently deposited sediments due to a reduced amount of dilution by calcite (Rowell, 1992).

6.4 Contaminant Inventory in Onondaga Lake

As extensively discussed in this report, the decades of industrial and municipal discharges to Onondaga Lake have thoroughly contaminated its sediments. As noted throughout this chapter, few contaminants have a significant flux to the lake outlet compared to the overall inputs. Thus, the majority of contamination delivered to the lake is retained within the lake and its sediments. Additionally, the direct deposition of wastes within the lake (i.e., the in-lake waste deposit) has further contributed to the contamination. Since the lake is effective at retaining contaminant releases, the lake bottom has become a reservoir for the contaminants. In the littoral zone where the waters remain oxic year-round and the sediments are subject to resuspension and bioturbation, the sediment inventory represents a potential source for continued contamination of lake water and biota.

The following analysis presents an estimate of the inventory of nine of the major CPOIs in the lake (note that the PCDD/PCDF database was not extensive enough to estimate a lakewide inventory). In compiling the lake's inventory, some perspective is provided on the magnitude of the historical discharges of these contaminants relative to the current sources and sinks. Additionally, the analysis serves to highlight areas with significant reservoirs of contamination. This section summarizes the inventories of the following CPOIs:

- Mercury.
- Cadmium.
- Chromium.
- Lead.
- Benzene.
- Chlorinated benzenes (sum).
- Dichlorobenzenes (sum).
- Naphthalene.
- PCBs.

A map of each contaminant is presented (Figures 6-37 through 6-46) based on mass-per-unit-area (MPA) estimates derived from the RI. MPA represents the total inventory of a contaminant contained within the sediment at a given sampling point. It is the integration of all measured concentrations at that location based on the sediment density and the length of the individual core segments. Thus, an MPA value is obtained for each coring location. In order to create the maps of contamination and integrate the total contaminant mass in the lake, each coring location is assigned an area based on a nearest neighbor approach. That is, the lake bottom is segmented into polygons such that a single core is contained within each polygon and all of the area within the polygon is closer to that coring location than to any other. The polygon is then assigned the

properties (i.e., MPA) of the core it contains. This technique is called Thiessen polygons, or polygonal declustering. By then multiplying each polygonal area by its associated MPA value and summing, an estimate of the mass of the contaminant in the lake is obtained. This technique is particularly useful for study areas with variable sampling densities, since samples are weighted by their associated areas. Thus, areas with high sampling densities are not overly weighted in the inventory estimate.

In constructing the MPA maps for the lake, consideration was given to the significant differences observed for littoral and profundal sediment areas. For this reason, the 9 m contour was used as a boundary in the analysis (as was done in the contaminant distribution maps presented in Chapter 5). Thus, littoral zone samples were only used to estimate littoral sediment inventories and profundal zone samples were only used for profundal sediment inventories. In estimating the MPA from the available data, it is recognized that these estimates may underestimate the actual local inventory in some instances. Specifically, if a core fails to obtain the entire sequence of contaminated sediment at a given location (e.g., a 2 m core is collected from an area with 3 m of contamination), the MPA value will be less than the actual inventory. Thus, the inventories presented represent minimum estimates for the mass of contamination in the lake.

Table 6-50 presents the mass inventory estimates for the nine compounds listed above. Lake inventories of contamination range from a maximum of 2.9×10^6 kg of chromium to 5,000 kg of low molecular weight PCBs. These inventories speak to the huge scale of the historical discharges to the lake. For example, the estimated 169,000 kg of mercury in the lake sediments represent a daily average load of 12 kg to the lake every day for a 40-year period. This can be compared to the values presented in Table 6-20, wherein the daily input mercury load for the 120-day period of stratification in 1992 was roughly 0.03 kg per day.

Mercury

Figure 6-37 shows the distribution of mercury mass in the lake sediments using the 1992 and 2000 sediment data obtained by Honeywell. The amount of mercury in the lake bottom was estimated at approximately 169 metric tons (Table 6-50). The mass of mercury in the lake sediments is relatively high and evenly distributed throughout the region below (deeper than) a water depth of 9 m, indicating that mercury is well distributed throughout the waters of the lake prior to capture by settling suspended matter. In the littoral zones, the highest MPA value was clustered around the in-lake waste deposit near Harbor Brook and in the Ninemile Creek area, consistent with the known sources in these areas. The northern section of shoreline has MPA values ranging from 0 to 1 g/m², indicating that little of this region is depositional.

Cadmium

The cadmium inventory in the lake bottom, as shown in Figure 6-38, was estimated at 126 metric tons (Table 6-50). Unlike mercury and chromium, the amount of cadmium in the southern deep basin is higher than the northern deep basin (see Figure 6-38), suggesting less homogenization of cadmium discharges prior to their deposition on the lake bottom. The highest amount of cadmium was found in the littoral zone
area extending from the Metro outfall to the mouth of Ley Creek. The Honeywell in-lake deposit area has a lower, but relatively homogeneous, cadmium mass.

Chromium

The amount of chromium in the lake bottom was estimated to be approximately 2,900 metric tons (Table 6-50). Figure 6-39 shows that chromium is widely and evenly distributed on the lake bottom in the deep basins suggesting that, like mercury, its discharges to the lake were relatively well homogenized in the epilimnion prior to the removal of chromium by particle settling. The highest inventories of chromium were found in the areas near Tributary 5A.

Lead

The amount of lead in the Onondaga Lake sediments was estimated to be about 1,900 metric tons (Table 6-50). The amount of lead in the lake bottom is widely distributed with the higher mass in the southern section of the lake (see Figure 6-40). The area of highest lead inventory extends from the in-lake waste deposit area to the mouth of Tributary 5A and near Onondaga Creek. Like mercury, the amount of lead in the northern littoral section of the lake is relatively low.

Benzene

The amount of benzene in the lake bottom was estimated at 9 metric tons (Table 6-50). Figure 6-41 shows the distribution of benzene mass on the lake bottom. The spatial extent of benzene is limited to the Honeywell in-lake waste deposit area and the rest of the lake has a much smaller amount of benzene, on the order of 0 to 1 g/m². This observation is consistent with its geochemistry, wherein volatilization and degradation are likely to limit its migration in the lake.

Chlorinated Benzenes

The amount of chlorinated benzenes (sum) in the lake bottom was estimated at approximately 147 metric tons (Table 6-50). Figure 6-42 shows the distribution of the sum of chlorinated benzenes mass on the lake bottom. From the figure, it can be seen that chlorinated benzenes are concentrated in the region around the Honeywell in-lake waste deposit. The rest of the lake has a much smaller amount of chlorinated benzenes, on the order of 0 to 1 g/m². This observation is consistent with its geochemistry, wherein volatilization and degradation are likely to limit its migration in the environment. The very high inventories off the Honeywell lakeshore area are consistent with the disposal of wastes in this area and the groundwater/DNAPL transport from the Willis Avenue site.

Dichlorobenzenes

The amount of dichlorobenzenes in the Onondaga Lake sediments was estimated to be approximately 92 metric tons (Table 6-50). Similar to the sum of chlorinated benzenes, the sum of dichlorobenzenes mass

is focused off the Honeywell lakeshore area (see Figure 6-43). This is consistent with the similar geochemistries and likely sources of these compounds.

Naphthalene

The amount of naphthalene in the Onondaga Lake sediments was estimated to be approximately 230 metric tons (Table 6-50). Figure 6-44 shows that the southern section of the lake contains the majority of the naphthalene mass. However, the sample coverage for naphthalene is much more limited than the other CPOIs examined here, as evident in the size of the polygons in the deep basins. Nonetheless, the data show the highest amount of naphthalene was found to be at the Honeywell in-lake waste deposit near the Wastebed B/Harbor Brook site, which is consistent with the Wastebed B/Harbor Brook site being a likely source of this contaminant. The pattern of the naphthalene in the Honeywell lakeshore area is similar to that of mercury and chlorinated benzenes, as might be expected, given the likeliness that the Honeywell facilities are the source.

Polychlorinated Biphenyls

The distribution of the PCB inventory in the lake is relatively unique. For both LPCBs and HPCBs, the deep basin inventory grades from the high inventories of the southern littoral zone boundary to background levels in the area near the lake outlet (see Figures 6-45 and 6-46). In the southern littoral zone area, PCB inventories are high in both the Honeywell lakeshore area and near the Ley Creek delta. Both areas have documented PCB sources, as discussed previously in Section 6.2.6 and in Chapter 4. Notably, for both PCB groups, the inventories are highest in the relatively deeper portions of the littoral zone, between 4 and 9 m in water depth. Areas closer to shore are frequently at background or near background levels. In the northern littoral zone, PCBs are elevated in the area of the Ninemile Creek delta. The amounts of LPCBs and HPCBs in the lake bottom were estimated at 7 and 5 metric tons, respectively (Table 6-50).

6.5 Fate and Transport Summary

The analysis of sources, transport, and fate of contaminants in Onondaga Lake included a thorough summary of existing information on the contribution of contaminants to the lake from upland sites associated with former Honeywell activities, an extensive analysis of the behavior of mercury in Onondaga Lake, and a detailed discussion of the status and anticipated fate of non-mercury CPOIs in the lake. The description of loading or potential loading of contaminants to Onondaga Lake from upland sites does not reflect current or potential remedial activities at these sites.

Based on the analysis of the transport and fate of the various CPOIs, several important conclusions can be drawn concerning the lake and its contamination, as follows:

• The lake is a sink for essentially all contaminants. For every CPOI examined, the flux of the contaminant to the lake outlet was small in comparison to the sum of

internal and external loads to the lake. Relatively little of the contamination delivered to the lake escapes the lake via the outlet.

Several important contaminant source areas or mechanisms have been identified. These transport routes serve to deliver multiple contaminants to the lake. Among the more important routes and mechanisms are the following:

- Ninemile Creek: This tributary has been and continues to be the single most important external source for total mercury. It has also been a source of PCDD/PCDFs, PCBs, lead, and chromium to the lake.

- Harbor Brook: This tributary has been and continues to be a major source of LPAHs, particularly naphthalene, to the lake.

- Ley and Onondaga Creeks: These tributaries appear to be ongoing sources of PCBs, and possibly PCDD/PCDFs, and are among the most important sources of lead to the lake.

- East Flume: This tributary has been a very important conduit for mercury, chlorinated benzenes, PAHs, and PCDD/PCDFs.

- Honeywell lakeshore area groundwater: Transport of contaminants to the lake via groundwater represents the most important loading route for several CPOIs, including LPAHs such as naphthalene (from the Wastebed B/Harbor Brook site), chlorobenzene and dichlorobenzenes (from the Willis Avenue site), and all four BTEX compounds (from the Willis Avenue, Semet Residue Ponds, and Wastebed B/Harbor Brook sites). The DNAPL plumes, which lie beneath the Willis Avenue and Wastebed B/Harbor Brook sites, contribute to the groundwater contamination and may also be contributing DNAPL directly to the lake.

- Honeywell in-lake waste deposit: Resuspension of these materials presents a potentially important source of mercury to the lake, perhaps representing the main internal source to the water column. It is also a potentially important source of PCDD/PCDFs and other CPOIs such as BTEX, chlorinated benzenes, PCBs, PAHs, and non-mercury metals. Surface concentrations of several CPOIs are highly elevated in these beds relative to the rest of the lake.

- **Profundal sediments:** These sediments appear to be responsible for the increase in the hypolimnetic mercury inventory during summer stratification. This increase is believed to be the source of dissolved mercury for production of methylmercury in the lake.

- The major contaminant loss mechanisms for the lake include settling of suspended matter (mercury, methylmercury, other metals, PCDD/PCDFs), volatilization (BTEX, chlorinated benzenes, PAHs, PCBs), and in-lake degradation (BTEX, chlorobenzene).
- The lake sediments represent a huge reservoir of contaminant mass for many other contaminants. However, significant inventories of contamination exist in the littoral zone near the Honeywell lakeshore area, extending along the shore as far as Ley Creek for some compounds. This inventory of contamination cannot be considered sequestered as it is in an area subject to wind-driven waves. Indeed, the in-lake waste deposit is located in this region, representing a clear source of contamination to the water column of the lake.
- The major external sources to the lake are well documented by the available data. The Honeywell facilities represent the major source of most of the CPOIs found in the lake (lead, cadmium, and chromium being the notable exceptions). In fact, several of the Honeywell CPOIs are sufficiently unique that they can be identified by standard statistical tests such as PCAs. These tools strongly implicate the Honeywell facilities as the primary source of two different contaminant types (i.e., LPAHs and PCDD/PCDFs).

Summary of Mercury Fate and Transport

Mass balances for total mercury and methylmercury were determined for Onondaga Lake during stratification in 1992. The total mercury input to the lake from sources identified in the RI/FS Work Plan during the period of stratification was estimated as 3,500 g, with the tributaries and Metro accounting for about 72 percent of the total mercury input to the lake and groundwater contributing approximately 22 percent. Of the tributaries, Ninemile Creek was clearly the most important, contributing 1,270 g, or half of the total tributary load. For methylmercury, tributaries and groundwater account for approximately 26 and 15 percent of the loading, respectively, to Onondaga Lake. Net methylmercury production (at least 52 percent of total input) accounts for the vast majority of the input to the lake. Methylmercury production occurs in anoxic waters (and sediment) so any factors that contribute to oxygen consumption during stratification will exacerbate methylmercury production.

The analysis of the mercury fluxes during the summer and fall and the mass balance during the stratified period suggests evidence for additional internal sources to the lake. The estimated loss of total mercury from the entire lake during the stratified period is about 11,000 grams of mercury. Only about 3,500 g of mercury inputs could be defined from sources identified in the RI/FS Work Plan, such as the tributaries and groundwater.

Closer examination of the mercury fluxes reveals an imbalance for both the epilimnion and hypolimnion. Both regions have greater mercury outputs than inputs, suggesting one or more sources to each region. For the epilimnion, a significant fraction of the "missing" total mercury input may come from resuspension of Honeywell waste materials deposited in the lake through the East Flume during the 1930s, 1940s, and 1950s. This waste forms a large delta in front of the Wastebed B/Harbor Brook area, contains some of the higher concentrations of mercury in the lake bottom, and is in an erosional area. Wind-driven suspension is a likely major mechanism for the release of contaminants from these deposits. Groundwater advection through these materials may also transport important quantities of mercury as well as other CPOIs to the lake.

The missing mercury input to the hypolimnion appears to be of the same magnitude as that for the epilimnion, based on the difference between the estimated inputs and outputs to each region. In this case, the profundal sediments appear the likely additional source, since other external sources to the region have largely been ruled out. Evidence for the release of dissolved-phase total mercury within the surficial sediments, as well as enhanced sediment-water exchange by resuspension due to methane ebullition provide likely mechanisms for release.

For both the epilimnion and the hypolimnion, the uncertainties regarding the missing inputs of mercury are chiefly associated with the magnitudes of the internal release and recapture of mercury within the lake, although the magnitudes appear to be similar in scale to the known inputs. Nonetheless, enough is known about the lake in general, and about possible release processes specifically, to identify the likely sources of the additional inputs for the purposes of this investigation: in the case of the littoral sediments, the elevated surface concentrations, the historical records, and the direct measurements of water column increases over the littoral sediments adjacent to the Honeywell site clearly identify this region as a major source of mercury to the epilimnion. Regardless of transfer process, this area probably represents the most important internal source of mercury to the epilimnion.

For the profundal sediments, studies completed by Honeywell have effectively eliminated all other possible sources to the hypolimnion. Thus, regardless of the transfer mechanism, the profundal sediments are the likely source of the hypolimnetic inventory increase, as well as the observed increase in the particle settling flux of mercury through the hypolimnion.

Processes in the lake tend to keep the total mercury in the epilimnion at a concentration of about 5 ng/L, primarily associated with particles. This is not significantly above the concentrations seen in the tributaries unaffected by Honeywell operations. However, in the hypolimnion, total mercury concentrations climb to about 25 ng/L during the stratified period and are primarily (50 to 90 percent) in the dissolved phase. As noted above, it is likely that the source of the mercury building up in the hypolimnion is the mercury released from the shallow profundal sediments, which are primarily comprised of recently deposited sediment. Porewater profiles from the profundal region of the lake were found to exhibit distinct concentration maxima in the surficial core segment, indicative of mercury release, further supporting this hypothesis. In addition, ebullition of methane gas enhances the transfer of materials from the profundal sediments to the hypolimnetic water column.

The ultimate fate of most (about 95 percent) the mercury entering the lake is associated with particles that settle to the bottom of the lake.

During fall turnover, the elevated amounts of total mercury in the hypolimnetic waters are rapidly removed from the water column, presumably precipitated along with iron and sulfide to the lake bottom, as the hypolimnetic waters are entrained into the oxygenated epilimnion. Notably, this process yields a residual water column concentration of about 5 ng/L, the same concentration present in the hypolimnion prior to the onset of summer stratification. This process also prevents the escape of the total mercury from the hypolimnion to the epilimnion.

The overall methylmercury budget for the lake during the stratified period is about 440 grams. Unlike total mercury, methylmercury is not conservative, and the mass balance is based on the net result of competing processes. The source of the majority (at least 52 percent) of methylmercury is from in-lake production with lesser amounts from the tributaries and Metro (26 percent) and porewater advection/diffusion (6 percent). The primary source of methylmercury production is in the water column in the hypolimnion. The zone of peak production migrates vertically and may be associated with the front of hydrogen sulfide diffusing upward from the sediments. The release of dissolved total mercury to the hypolimnion during stratification is believed to supply much of the mercury for methylmercury production, since production is considered dependent on the dissolved concentration of mercury. Diffusion of methylmercury from the hypolimnion during stratification.

Processes in the lake tend to keep methylmercury at concentrations less than 1 ng/L in the epilimnion and primarily associated with particles. In the hypolimnion, the peak concentrations are about 15 ng/L, primarily (50 to 100 percent) in the dissolved phase. During fall turnover, the elevated amounts of methylmercury in the hypolimnetic water are entrained into the epilimnion causing the epilimnetic concentrations to rise rapidly from 0.9 to 2.7 ng/L, tripling the concentration in the top 6 m of the lake. A mass balance performed for the 1999 fall turnover event showed that more than half of the hypolimnetic inventory of methylmercury was displaced into the epilimnion above 9 m in water depth, greatly increasing the available methylmercury in the biologically important region of the lake. The removal of the methylmercury is not as rapid as the total mercury, and the concentrations of methylmercury in the oxic zone remains elevated for at least several weeks.

One of the impacts from mercury contamination is the occurrence of elevated concentrations of mercury in fish and benthic organisms. Most species of fish in Onondaga Lake have elevated concentrations of mercury compared to fish in other bodies of water. The dominant form of mercury in fish flesh is methylmercury, suggesting that the fish must be exposed to sources of methylmercury in the lake.

Summary of Fate and Transport for Non-Mercury CPOIs

Included among the non-mercury CPOIs are metals, BTEX, chlorinated benzenes, PAHs, PCBs, and PCDD/PCDFs. The distribution of these CPOIs in the sediments (Figures 6-37 through 6-46 and Chapter

5, Figures 5-2 to 5-27) reflects the historical disposal into the lake and ongoing discharge from groundwater and surface water. The highest concentrations of all these compounds in lake sediments are typically found in the littoral zone adjacent to the Honeywell facilities, demonstrating the impact of those facilities on the lake for those CPOIs. For some of the CPOIs, the maps also indicate additional historical sources. PCBs also have high concentrations near the mouth of Ley Creek, perhaps related to the releases of PCBs from the GM – IFG site and other facilities in that basin. The PAH maps suggest an additional source between Ley Creek and Onondaga Creek, perhaps the former Oil City facilities. Some of the metals which had widespread use, such as lead, have widespread distributions in the lake as well.

The largest ongoing source of metals into the lake is from tributary loads (on the order of 1,800 for chromium to 3,000 kg/yr for lead), with Ninemile Creek contributing a proportionally larger load of chromium than the other tributaries. The most likely fate of the metal CPOIs is settling to the bottom of the lake on particles. Based on measurements of sediment cores from the lake bottom, the loadings of metals to the lake have greatly deceased since the 1960s. It is expected, although it was not examined in the cores, that loads of other contaminants have greatly decreased since that time as well.

The primary source of BTEX to the lake is via groundwater originating on the Willis Avenue and Semet Residue Ponds and the Wastebed B/Harbor Brook sites. The in-lake waste deposit is also suspect as a source but no data are currently available to quantify this input. The primary loss of BTEX from the lake appears to be via volatilization. However, like many of the fluxes for BTEX, this estimate is hampered by the lack of detectable concentrations in lake media. Nonetheless, this loss term is consistent with the geochemical nature of this relatively volatile group. Although it cannot be directly estimated here, losses via microbial degradation and photolysis are also likely for this group and probably represent a significant sink for BTEX as well. Overall, inputs of BTEX to the lake appear quite large (on the order of 11,000 kg/yr) but the estimates of both inputs and losses are hampered by the sensitivity of the available data.

By at least an order-of-magnitude, the largest ongoing source of chlorinated benzenes into the lake is from groundwater associated with the Honeywell facilities. In addition, there is evidence of a DNAPL chlorinated benzene plume near the lakeshore which is certainly affecting the groundwater and, in turn producing elevated sediment concentrations of chlorinated benzenes. If this DNAPL is migrating directly to the lake, the inputs could be much higher than estimated. Based on the loading calculations, the most likely fate of the chlorinated benzenes upon entering the lake is either volatilization or outflow from the lake. However, the hydrophobic nature of the more highly chlorinated benzenes would suggest that adsorption to particles with subsequent settling is also important. The loading estimates indicate a large discrepancy between the inputs (on the order of 7,000 kg/yr for all chlorinated benzenes) and the estimated outputs (on the order of 500 kg/yr), suggesting that either at least one the fluxes is not well constrained or that an additional loss mechanism is not accounted for.

The largest ongoing source of PAHs into the lake is from groundwater associated with the Honeywell facilities, followed by diffusion from the in-lake waste deposit in front of Wastebed B/Harbor Brook, and then by contributions from the tributaries. However, there is evidence of a DNAPL naphthalene plume near the lakeshore, as well as beneath Harbor Brook, which is certainly affecting the groundwater in this area

and the surface water in Harbor Brook. Like the chlorinated benzenes, if this DNAPL is migrating directly to the lake, the inputs could be much higher than estimated. The most likely fate for the LPAHs is volatilization, while settling to the lake bottom is likely important for the HPAHs. Examination of the sediment data using PCA and a comparison to compounds unique to Honeywell, indicate that Honeywell is the primary source of LPAHs to the lake.

The mass loading of PCBs is relatively small (less than 100 kg/yr) compared to the other CPOIs. However, the high rate of bioaccumulation of PCBs causes it to be of great significance in terms of contamination of fish flesh. Based on the presence of PCBs in their sediments, the tributaries appear to be the major on-going sources to the lake. In particular, Onondaga Creek (Aroclor 1260) and Ley Creek (Aroclors 1016, 1242, and 1260) appear to be the most important. PCBs are also released from the sediments via resuspension but this appears to be a much smaller flux than that delivered by the tributaries. Losses of PCBs from the lake occur primarily by volatilization and particle settling. Within the sediments, limited biodegradation is likely but has not been reported to date. Biological exposure is an amalgam of loads and existing PCB inventory since there are several exposure pathways. Thus, it is unclear whether historical or recently discharged PCBs are responsible for elevated PCBs detected in biota.

PCDD/PCDFs have been found in sediments in the area of the Honeywell in-lake waste deposit near the East Flume, and fish in close contact with the sediments (carp and catfish) collected from this area show significantly higher concentrations of PCDD/PCDFs. Inferring from tributary sediment concentrations, ongoing discharges to the lake via the East Flume, Ninemile Creek, and potentially Ley Creek represent the largest contributors of PCDD/PCDFs to the lake (about 13 g/yr). The nature of these discharges suggests that the potential Ley Creek source is OCDD-dominant, the Ninemile Creek source is OCDD-and TCDF-dominant, while the East Flume is TCDF-dominant. Other sources of a similar magnitude are resuspension of the in-lake waste deposit and atmospheric deposition. Once in the lake, PCDD/PCDFs tend to adhere to particles where they settle to the bottom, and remain on the sediments where they are available for biological uptake. Historically, it appears that both OCDD-dominant and TCDF-dominant discharges have originated from the Honeywell facility. Of these, the TCDF-dominant releases from the Honeywell lakeshore area would be of greater concern environmentally because of their high degree of toxicity.

Honeywell discharged ionic (Solvay) waste into Onondaga Lake for about 100 years. Different methods (sediment traps and high-resolution cores) have been used to estimate the impact that this discharge has had on the precipitation of calcite in the lake. These analyses suggest that the calcite precipitation rate at least doubled during the time that Honeywell operated. Currently, ionic concentrations remain elevated with respect to other nearby water bodies, but overall, ionic concentrations in the lake water have been drastically reduced from conditions in the 1980s and earlier.